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Editor's Outlook

ALAS, THE MOLECULE!

WHAT has happened to our old friend, the molecule? We don't see him as often as we used to. At best, he has become a pretty nebulous conception, for it is only in the least tangible state of matter that we can be sure of his permanent existence.

Most of us who learned our first chemistry years ago were supposed to be satisfied with the idea that "a molecule is the smallest unit of a compound substance that would have the properties of the substance," or merely "the smallest unit of a compound substance (period)." But those were the days (God bless' em) when you couldn't poke around among these units and feel their edges and corners, so to speak. Now you can practically stick a molecule on a pin and look at it from all sides, top and bottom.

Strangely, in the face of all that we have learned, the old, outworn definition still persists in some of the latest textbooks. Certainly there are few, if any, physical properties which can be conceived as inherent characteristics of individual molecules. In most cases they are the result of the *arrangement* or relation between molecules or of the forces between them. Hardness, for instance, cannot be thought of as a property of an individual molecule, nor can melting or boiling points or other thermal properties. Even temperature, which, although not a property, has always been closely related to disorderly molecular motion, has no meaning when applied to a single molecule.

Only in a rather idealized way can the chemical properties of a substance be conceived as functions of individual molecules. TNT is "explosive," but I dare say that the decomposition of a single molecule, if we could watch it, would appear entirely different from what we ordinarily think of as an explosion. The very names which we apply to some of our chemical properties imply the presence of many molecules.

After all, the properties of rubber can scarcely be ascribed to the isoprene molecule itself—or the butadiene, or styrene, or isobutylene, or whatever you make the "rubber" out of. And what *is* the molecule of rubber, anyway? We do not even know very surely how big it is.

And, of course, the situation is just as intangible in the case of simple inorganic salts, for a different reason. It is easy to justify writing the *formula*, NaCl, but completely impossible to justify its significance as a *molecule*, for you cannot find any such thing in the salt crystal. Perhaps there are a very few such "ion pairs" when you dissolve it in water, maybe there are some in the fused material, but only when you vaporize the stuff can you be very sure that you have any real NaCl molecules—and who wants to fool around with *gaseous* salt!

One well-known textbook uses the term "practical molecule" for the dubious practice of giving real molecular significance to a conventional formula. But what is there "practical" about it when it won't *work*? It is merely a "loose-thinking molecule," and quite as indefinite as speaking of a "couple of people," which may indeed be a closely snuggled pair walking arm in arm, but may, on the other hand, be two persons joined only in the fact that they were both pedestrians killed in the same auto accident.

We would be better off if we defined our molecules in terms of the atoms which compose them rather than in terms of the substances of which they are sometimes the units. For time has made us much more aware of the existence, significance, and properties of atoms than of molecules. The molecule occupies a much less stable position in the structure of matter than does the atom. At one time the terms "atom," "compound atom," and "molecule" were pretty confused and tangled up. Perhaps it is unfortunate that we didn't keep the term "compound atom" instead of giving it up for "molecule," because that is what we really mean—a group of atoms which behaves as an independent unit. (All right, suppose it *is* electrically charged; atoms are frequently positive or negative, as a result of their own internal structure, and when they group together, they do not always do so in such numbers as to neutralize each other. A complex "ion" is merely a special name for a charged molecule.)

Dalton's atomic theory had its defects, particularly the assumption that all the atoms of an element are alike in mass. Another defect, as it is usually interpreted, is that in chemical combination the atoms of one element always unite *individually* with atoms of another element to form molecules of compounds. However, when sodium unites with chlorine, we cannot very well picture each sodium atom hunting around for a partner, taking her by the arm, and sitting down in a corner of the salt crystal. There are no chummy "twosomes" at this party; they are all sitting sedately in rows—boy, girl, boy, girl, boy, girl. . . .

Well, how about liquids? Take water, for instance (most of us do!). There are independent molecular units here, to be sure, but just which ones are they, and where? "Hydrogen bonding" is what keeps it from being a simple, easy picture—the basis for "as-

(*Continued on page 458*)

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GENUINE AND SYNTHETIC Rubies

A GREAT many miracles of synthesis have been achieved since World War I. In some instances wholly synthesized products, having chemical compositions entirely different from their counterparts in nature, have been formulated to yield similar or identical end results. Quinine would be an example.

Probably the best example of reproducing nature at its best is the preparation and manufacture of ruby and sapphire. Here we have a man-made product that is practically identical by every chemical and physical standard with the genuine material. The resultant gem is in some cases so "perfect" that careful scientific tests must be applied in order to differentiate the genuine from its synthetic counterpart.

It is unfortunate that to the layman the terms "synthetic" and "imitation" are synonymous. A high-index red glass might simulate a ruby when facetted, but it is still an imitation. Synthetic corundum, however, is not an imitation of the genuine species.

The manufacture of synthetic corundum, since the time of Verneuill (1856–1913), is well known and has been widely reviewed in the literature. To those who are not acquainted with the process a brief résumé is given.

All ruby and sapphire, whether genuine or synthetic, is composed of aluminum oxide—the hexagonal form of alpha corundum. There exist other forms of alumina, as beta, gamma, etc., but these transitional species are of greater importance to the ceramic engineer than to the manufacturer of synthetic gemstones.

Strange as it may seem, synthetic ruby and sapphire are not produced from alumina derived from bauxite but from the alumina obtained from the precipitation of ammonia alum (*1*, *2*). The entire success of the process depends upon the careful preparation of the alumina. Alumina with a chemical composition of 99.99 per cent is not good enough to produce gem quality corundum. The raw material prior to fusion must be free from traces of other elements. For example, translucency rather than transparency might

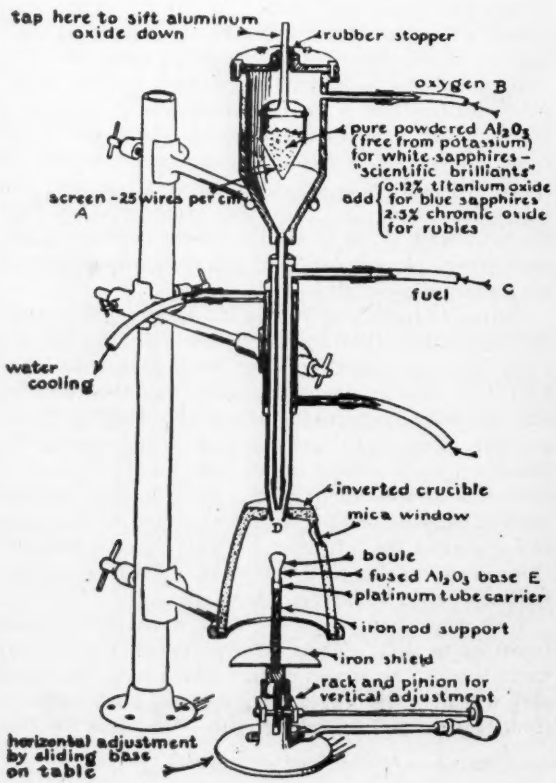
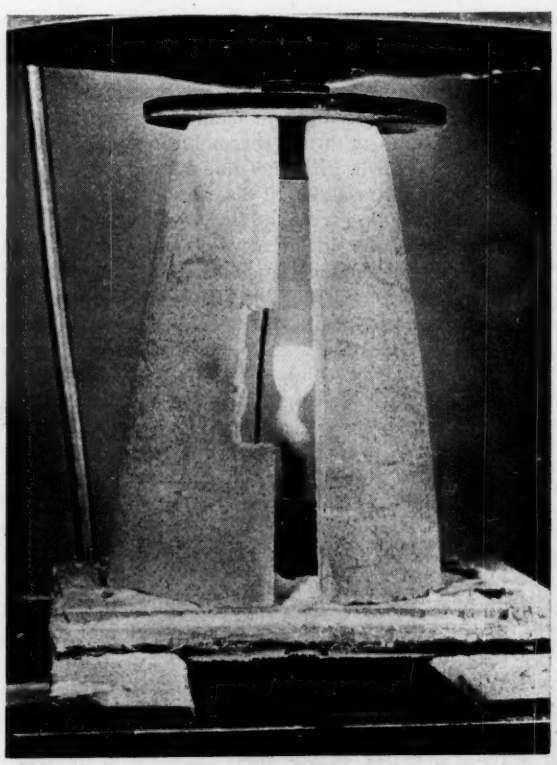


FIGURE 1. VERNEUILL'S HIGH TEMPERATURE FURNACE FOR MAKING SYNTHETIC RUBIES AND SAPPHIRES



(Courtesy of Linde Air Products Company)

FIGURE 2. WHITE HOT BOULE SURROUNDED BY HIGH-TEMPERATURE REFRACTORY CRUCIBLE

AND Sapphires

A. E. ALEXANDER
Gem Trade Laboratory, Inc.,
New York, New York

result, as well as the formation of undesirable characteristic colors.

To fuse the raw material, a modification of Verneuill's high-temperature furnace is generally employed, in this country as well as abroad (Figures 1 and 2). A quantity of finely divided powder is placed in the "hopper" and periodically tapped to permit a small amount to pass through screen *A*.[1] Hydrogen and oxygen, in proper proportions, are usually used as "fuel." The oxygen enters *B*, the hydrogen through *C*. Note that the powder descends down the oxygen outlet. Intense temperatures, of the order of 4500°F., are generated at *D*, with the result that the descending powder is instantly melted on passing through the flame. The molten globule falls on a ceramic pedestal *E*, and a mass is built up, known in the industry as a "boule" (Figures 3 and 4). Boules up to 750 carats and larger have been produced, although in production 300 carats is the usual size. A carat, as the standard unit of weight in the jewelry trade, weighs 0.20 g. The price per carat of colorless (referred to in the trade as "white") sapphire is at this writing three cents.

In addition to white sapphires, colored stones of wide variety have been produced for the jewelry trade. Ruby color is obtained by the addition of chromium oxide, up to 2.5 per cent. Lesser amounts of the oxide will yield varying shades of pink and red. Blue sapphire, as manufactured in Europe (but not commercially available in the United States), is produced by a fraction of one per cent of titanium oxide or cobalt oxide. Ravier, Gordon, and Smith discuss the compounds that are generally used to produce color variation in corundum (*2, 3, 4*). The entire procedure is not as simple as outlined here or as one might gather from perusing the literature on the subject. Many secret processes and techniques have undoubtedly been evolved.

One other synthetic gemstone is manufactured here and abroad—the synthetic magnesium aluminate, spinel (*4. 5*). This material resembles blue sapphire on casual inspection; the chemical and physical properties, however, differ from the spinel found in nature. Since this material is not morphologically related to either synthetic or genuine corundum, we will not discuss it further.

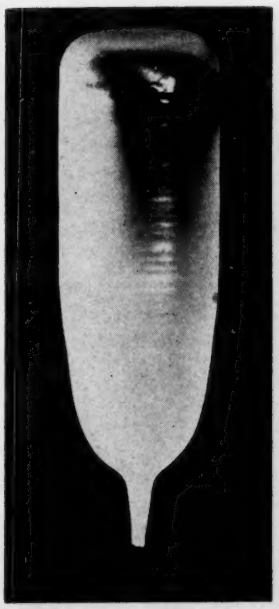
Prior to World War II the Swiss, French, and Germans manufactured great quantities of synthetic corundum—amounts said to aggregate 750,000 carats per day (*14*). The most important industrial use of this material is for jewel bearings of watches, meters, and aircraft instruments. Cut and cabochon rubies and sapphires represent the next largest outlet for synthetic corundum.

The United States, as well as Great Britain, finding themselves cut off from this essential item, struck out on their own to reproduce the foreign process. The Linde Air Products Company not only met the challenge but before V-J day arrived far surpassed the continental Europeans in technical developments and methods of manufacture. The General Electric Company, Ltd., and the Smith Clock Works Ltd., of Great Britain also succeeded in processing fine synthetic corundum.

Before discussing the ways and means employed for differentiating the synthetic material from the genuine stone, let us review the more significant characteristics of the two types of corundum.

CHARACTERISTICS OF SYNTHETIC CORUNDUM

Three important physical characteristics feature synthetic ruby and sapphire. The first and most conspicuous is the formation of *curved* lines. These lines are created during the formation of the boule—that is,



(*Courtesy of Linde Air Products Company*)

FIGURE 3. A PERFECT BOULE OF RUBY AS MANUFACTURED TODAY

(*Courtesy of Linde Air Products Company*)

FIGURE 4. SPLIT BOULE SHOWING TYPICAL FRACTURED SURFACE. BOULES SPLIT EASILY BECAUSE OF INHERENT STRAIN

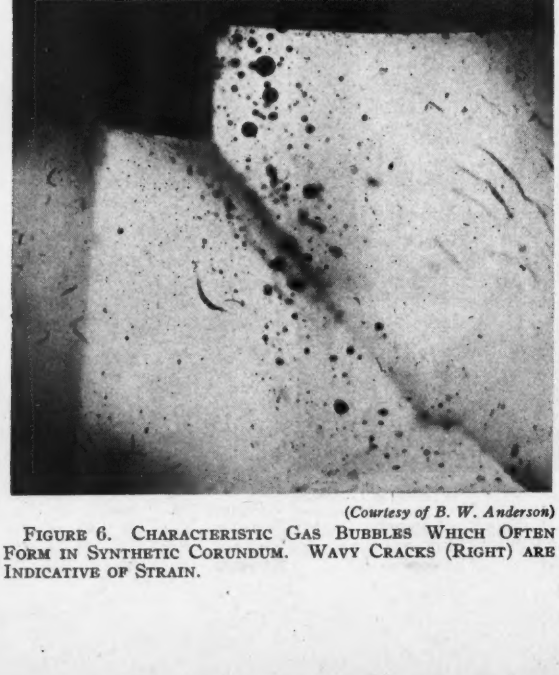
[1] The alum crystals are fired in a silica tray in a gas or electric furnace to 1000°C for about two hours. The charge swells up considerably and finally results in a sponge-like mass of gamma alumina. It is this material which is pulverized and later placed in the Verneuill furnace (*15*).

(*Courtesy of B. W. Anderson*)

FIGURE 5. TYPICAL CURVED FORMATIONAL STRUCTURE CHARACTERISTIC OF SYNTHETIC BLUE SAPPHIRE

the molten drop of alumina at regulated intervals piles up until a finely layered mass of corundum results. These lines are very conspicuous in synthetic ruby. Sapphire on the other hand presents, in a number of instances, a variation of the curved line structure seen in ruby. Curved color bands tend to form rather than numerous thin lines (Figure 5). The reason for this difference probably lies in the nature of the coloring agent, which also acts as a flux.

The fusion point of alumina can be lowered several hundred degrees by the incorporation of a flux, such as beryllium oxide, or a combination of fluxes. One of the more active fluxes is chromium oxide (Cr_2O_3). This compound also succeeds in lowering the melting point of alumina, making it exceedingly fluid. The effect is less pronounced in the case of the blue sapphire where the flux is said to be titanium oxide. In the first instance the greater fluidity produces lines which form quickly on contact; in the second case the molten drop is more viscous and sluggish, with the result that a band rather than a "line" results.



(*Courtesy of B. W. Anderson*)

FIGURE 6. CHARACTERISTIC GAS BUBBLES WHICH OFTEN FORM IN SYNTHETIC CORUNDUM. WAVY CRACKS (RIGHT) ARE INDICATIVE OF STRAIN.

Theoretically it should be possible to eliminate the formation of lines entirely. This could be done by adjusting the time-temperature relationships, by carefully controlling the atmosphere of the furnace, and by experimenting with different flux combinations.

The second characteristic of synthetic corundum is the formation of gas bubbles. Trapped gases, which may already have been included in the descending drop or subsequently produced when the drop makes contact with the stationary mass, yield additional discriminatory evidence. The bubbles, usually quite small, are invariably round. They may occur singly or in clouds, the latter consisting of hundreds of minute specks requiring greater magnification to discern (Figure 6). However, not all boule material yields gas bubbles, and in a few exceptional cases the gas bubbles may not be wholly spherical.

Lastly, synthetic corundum, on cooling, invariably crystallizes in a state of strain. Attempts by scientists of the I. G. Farbenindustrie laboratories, for example, to eliminate strain by hours of annealing at elevated temperatures proved futile (*6*). Observations with polarized light disclose the strain.

CHARACTERISTICS OF GENUINE CORUNDUM

The chief distinctive features of genuine rubies and sapphires fall into two categories—inclusions and crystallographic structures. The former may appear as rutile needles and other mineral species, "canals," iron stains, "feathers," irregularly shaped gas bubbles, and liquid inclusions of great diversity of form and habit (Figures 7 and 8). The crystallographic structures—the straight lines which instantly characterize the gem as genuine—represent the "zoning" of mineralogical terminology. Twinning planes may also be seen in gem corundum (Figure 6).

Burma rubies and sapphires are often characterized by the presence of rutile (TiO_2) needles which intersect at 120 degrees. A ruby or sapphire containing a heavy concentration of rutile needles gives a certain sheen to the gem. Again, sapphires may be clouded with "canals," now believed by mineralogists to be microscopically small tubules which likewise intersect at 120 degrees. The sheen effect, which is strictly an optical phenomenon, is referred to as "silk" in the jewelry trade.

The presence of the "canals" is of considerable importance to the jeweler, for such a gem when shaped into a curved form, known as the cabochon, will yield a six-rayed star or asterism, which is best observed in strong artificial light. We then have the well-known star sapphire of commerce, and in rarer instances, the star ruby.

Both genuine rubies and sapphires are rarely "clean." Nature, anticipating man's desire to duplicate and reproduce, has developed identifying criteria in the corundum minerals. On examining a paper of 100 cut rubies and sapphires from Burma and Siam, for example, a great variety of microscopic patterns is revealed—lines, cracks, cavities, and inclusions.

The interested reader should consult the articles and texts written by Anderson, Michel, and Gubelin who have taken many superb photomicrographs of gem corundum which vividly reveal the distinctive criteria of these fascinating minerals (*7*, *8*, *9*).

DISTINGUISHING THE SYNTHETIC GEM FROM THE GENUINE

Just as the medical radiologist interprets a radiograph with accuracy and intelligence, so must the gemologist be able to recognize and interpret the evidence within the gemstone which his physical equipment discloses.

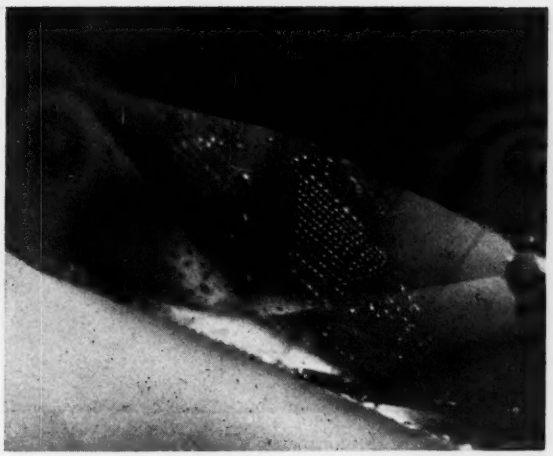
By far the most important instrument in the gemologist's laboratory is the stereoscopic binocular microscope. The refractometer, used for measuring refractive indexes, the dichroscope, designed to detect di- and trichroism, and the absorption spectroscope for disclosing the chromatic characteristics of the light transmitted by a colored stone, are all valuable tools in the gemologist's laboratory. A petrographic microscope is also a useful instrument in any mineralogical laboratory, particularly for examining powdered materials suspended in immersion liquids of known refractive index. It is valuable for examining unmounted gems at higher magnifications, but when a stone is mounted, as in a ring, clip, or brooch, difficulties arise because the gem cannot be turned freely for inspection.

The specific chemical and physical properties of both genuine and synthetic corundum are, for all practical purposes, identical (*1*, *10*).

	Genuine	*Synthetic*
Chemical formula	Al_2O_3	Al_2O_3
Specific gravity	3.99	3.99
Hardness (Mohs)	9	9
Hardness (Knoop) (*11*)	...	Perpendicular to *c*-axis, 1525–1660
	...	Parallel to *c*-axis, 1670–2000
Melting point	2030°C.	2030°C.
Crystal system	Hexagonal	Hexagonal
Indexes (n_D) (*4*)	1.759	1.760
	1.768	1.769

We must therefore fall back on whatever one can see within the gem itself, using the binocular microscope (Figure 9). In viewing any gemstone, especially one with a high index of refraction, it is best to immerse the gem in a liquid of high refractive index, such as monobromonaphthalene. The annoying internal reflections are greatly reduced, with the result that the minute inclusions and other criteria of both the genuine and the synthetic stone are more readily discernible.

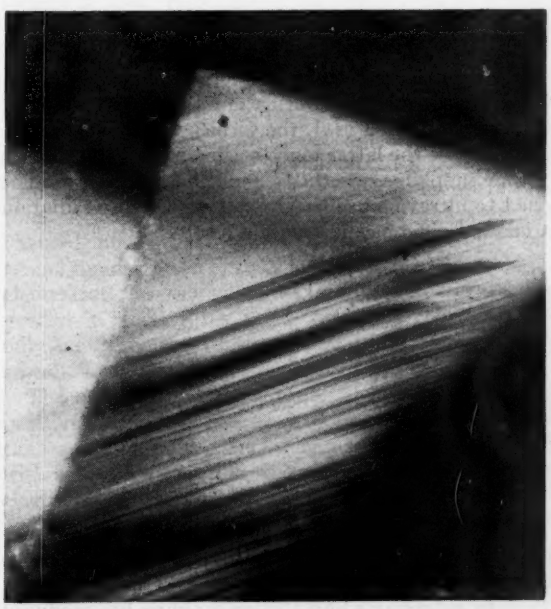
The hand absorption spectroscope, used in conjunction with a monocular microscope and proper illumination (*7*), is very useful in examining certain species of gemstones. Both the genuine and the synthetic ruby yield a narrow line (which may be resolved into two lines on close inspection) in the deep red and three lines in the blue part of the spectrum: 6942–6928 A. U. and 4680–4750 A. U. (*7*, *12*).



(*Courtesy of B. W. Anderson*)

FIGURE 7. "FEATHER" STRUCTURE IN GENUINE SAPPHIRE. THREE PARALLEL LINES REPRESENT TWINNING.

In the case of the blue sapphire a difference exists which permits distinguishing the genuine from the synthetic. A narrow line, wider than the lines seen in the ruby (which also may be resolved into two lines on close examination), occurs in the blue part of the spectrum at 4500 A. U. No synthetic sapphire shows a line or band in this region, according to Anderson (*7*). Webster (*12*), however, cautions on the use of this particular indicator, stating that some genuine sap-



(*Courtesy of B. W. Anderson*)

FIGURE 8. STRAIGHT COLOR BANDS, INDICATIVE OF A GENUINE SAPPHIRE

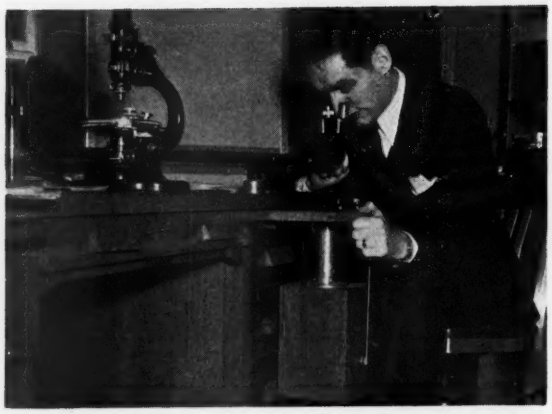


FIGURE 9. EXAMINING INTERNAL STRUCTURE OF GEMS (BINOCULAR MICROSCOPE WITH VERTICAL ILLUMINATOR)

phires may not reveal the band at 4500 A. U. By using larger, more accurate spectroscopic equipment, it is possible to bring out in sharp relief the narrow lines and broader bands produced by the colored stone under examination.

Two valuable aids in the gemologist's laboratory are X-ray and ultraviolet fluorescence. Many gemstones are not affected by these radiations; on the other hand, certain important gemstones are—for example, the corundums.

Genuine Burma rubies (if we assume that all rubies containing rutile needles come from Burma) fluoresce conspicuously when subjected to ultraviolet radiation. The phenomenon is best observed with a Hanovia quartz utility lamp in conjunction with a special Corning Glass ultraviolet filter.

Siam rubies are usually inert to ultraviolet radiation, although some variants may fluoresce slightly. When the same stones (from Burma and Siam) are subjected to X-ray radiation (*13*), the former will fluoresce brilliantly while the latter tend to remain dark.

Blue sapphires, whether genuine or synthetic, do not react to ultraviolet radiation, but with X-ray radiation a marked difference in reaction results:

Gem	*Kind*	*Origin*	*Fluorescence*
Sapphire	Genuine, blue	Ceylon	Dull red
Sapphire	Genuine, blue	Cashmere	Dull red
Sapphire	Genuine, blue	Australia	None
Sapphire	Genuine, blue	Montana	None
Sapphire	Genuine, blue	Burma	None
Sapphire	Genuine, blue	Siam	None (some varieties very faint)
Sapphire	Genuine, yellow	Not known	Medium
Sapphire	Genuine, white	Not known	None
Sapphire	Synthetic, blue	Swiss	Medium bright Dull red
Sapphire	Synthetic, pink	American	Brilliant red
Sapphire	Synthetic, orange-red	American	Brilliant orange-red

The writer has tested a great many synthetic sapphires and in every case has encountered a fluorescence that is conspicuous and distinctive in its coloration. To date, no genuine blue Ceylon sapphire has produced a fluorescence that could be confused with the effect observed in synthetic sapphire corundum.

When the phenomenon of fluorescence is used in conjunction with such other tests as the gemologist would ordinarily employ, positive identification of the stone under test becomes possible. The effect is best observed by placing the gemstone five inches from the X-ray tube target. The writer uses an X-ray tube equipped with a tungsten target. Ninety kilovolts and five milliamperes suffice to produce instantaneous fluorescence. The intensity is greater if a current of 10 milliamperes is used. A special lead-lined, ray-proof, light-tight viewing box is employed for all visual X-ray examination (Figure 10).

X-ray diffraction and X-ray spectrometric methods are other means of obtaining information on the structural differences of genuine and synthetic corundum. Unfortunately, these methods are time consuming and do not lend themselves to rapid analysis. Orienting the gem with respect to the crystallographic axis of the mineral and of aligning it with respect to the X-ray beam and the relatively long time of exposure, places these techniques in the category of applied research rather than in the realm of mass production. The jeweler who comes to the gemologist's laboratory with several pearl necklaces and a half dozen gemstones wants to know what he has in a matter of minutes, not hours.

Since the physical properties of both types of corundum are substantially identical, one would expect the lauegrams derived from these materials to be identical. Actually, according to preliminary work done in this field, they are not. It was found that genuine ruby

(*Continued on page 459*)

(*Courtesy of Tiffany & Company, Inc.*)

FIGURE 10. RADIOGRAPHIC AND FLUOROSCOPIC X-RAY UNIT USED TO TEST GEMSTONES AND PEARLS

Nuclear Reactions

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This is the second of a series of articles, written by Oak Ridge scientists, on the chemical significance of modern nuclear science and technology.

MODERN science has more than realized the alchemist's dream of transmutation. This has been accomplished by a successful attack on the nucleus, the ultimate determinant of the ordinary chemical and physical properties of the atom. Reactions involving nuclei and the fundamental "particles" of matter (*1*) are now commonplace.

A nucleus X is most simply characterized by a statement of its atomc number, Z, and its mass number, A. This information is frequently abbreviated ${}_{Z}X^{A}$. The forces which hold a given combination of protons and neutrons together will be discussed in the next article of this series. For our present purposes it will be sufficient to say that some combinations are unstable and decompose to form more stable combinations. This process is commonly called decay and obeys a first-order rate law. The decay rate, usually stated as half-life, and the mechanism of decay will be characteristic of the particular nucleus involved.

Some 273 stable nuclei occur naturally, and many more unstable nuclei are known. Most of the unstable nuclei do not occur naturally but must be synthesized by reactions such as those described below.

It is common practice to distinguish between nuclear transformation processes which involve half-lives of measurable length and those which to all appearances happen instantaneously. In this latter class fall the reactions which take place when nuclei are bombarded with various types of projectiles. The aggregate which is formed when a nucleus captures some particle, even though another particle may be immediately emitted, is a nucleus in every sense of the word and is called a "compound nucleus" to distinguish it from its longer-lived counterparts. Therefore nuclear bombardment reactions, by which most radioactive nuclei are made, can be regarded simply as very energetic and extremely short-lived cases of radioactive decay following external excitations.

The nomenclature of nuclear reactions is briefly as follows: The atomic number and mass number of each particle involved are given in the manner indicated above. The reaction is said to be balanced when the sum of the mass numbers of the reactants is equal to the sum of the mass numbers of the products, and similarly for the atomic numbers. The radiations (gamma and X-rays) accompanying the reaction are important phenomena having, of course, no mass or atomic numbers. Table 1 gives the mass and atomic numbers for the elementary particles and for a few common nuclei.

TABLE 1

ATOMIC AND MASS NUMBERS

Name	*Symbols*
Electron	${}_{-1}e^{0}$, β^{-}
Positron (positive electron)	${}_{+1}e^{0}$, β^{+}
Neutron	${}_{0}n^{1}$, n
Proton	${}_{1}H^{1}$, p
Deuteron	${}_{1}H^{2}$, d
Alpha particle	${}_{2}He^{4}$, α
Copper isotope	${}_{29}Cu^{63}$
Uranium isotope	${}_{92}U^{238}$

A typical nuclear reaction might be written as follows:

$$ {}_{4}Be^{9} + {}_{1}H^{1} \rightarrow {}_{3}Li^{6} + {}_{2}He^{4} + \gamma(\text{gamma ray}) $$

NUCLEAR PROJECTILES

If nuclear physics and chemistry were confined to the few naturally occurring radio-elements, it would indeed be a limited field. These occur chiefly at the extreme end of the periodic system, far from the elements which are most useful and interesting to the ordinary chemist. It has now become possible, by means of artificially induced nuclear reactions, to produce useful radio-isotopes of almost every known element.

Atomic nuclei are very small, positively charged, and held together by forces of enormous magnitude. These facts make the process of nuclear transformation difficult and inefficient. A particle which is to react with a nucleus must first be lucky enough to hit it; second, be energetic enough to cause the desired reaction; and third, if it is positively charged, must overcome the electrostatic repulsion of the nuclear charge. The uncharged nature of the neutron makes it a very useful projectile, although until the development of the chain-reacting pile, a rather scarce one. It is obtained only as a product of nuclear transformation and several types of sources are listed in the section on Nuclear Reactions. Considerable skill has been developed in the use of protons, deuterons, and alpha particles as positively charged nuclear projectiles.[1] They are readily obtained by ionization of their atomic forms,[2] followed by electrostatic acceleration. The tremendous energies needed in nuclear reactions with these particles can only be obtained with complicated and expensive devices, a few of which are mentioned below.

The potential difference required in accelerations of positively charged nuclear projectiles is usually more than a million volts. Such magnitudes can be reached with a *Van de Graaff Generator*, which builds up a static electricity charge on a sphere several feet in diameter. *Transformers in cascade*, with the secondary of the first

[1] Electrons and gamma rays find limited use as nuclear projectiles. They may be obtained as radioactive decay products or by "artificial" means related to the types described here for positive particles.

[2] "Natural" alpha particles, produced in radioactive decay, are also used as nuclear projectiles.

operating the primary of the second, and so on, can be used. The hazards and difficulties connected with maintenance of such extreme potential differences are serious drawbacks.

Lower operating potentials can be used to obtain the desired acceleration if the ions are directed to pass through the same potential difference several times. In a *linear multiple accelerator* a series of accelerating electrodes are arranged along the ion path and their potentials alternated at an interval corresponding to the time of flight of an ion from one gap to the next. A given group of ions thus finds itself subjected to the same accelerating potential each time it moves from one electrode to the next, and the net result is an energy corresponding to several times the actual operating potential; however, the length and number of electrodes become prohibitively great for very large energies.

The *cyclotron*, probably the most successful type of positive ion accelerator, also utilizes the principle of multiple accelerations through a relatively low potential difference; however, by superimposing a magnetic field perpendicular to the surface of the accelerating electrodes, the ions are made to travel in circular paths. The potential between the two electrodes is alternated at a rate such that each time a group of particles crosses the gap between plates, it is accelerated. Again particles with energies corresponding to many times the operating potential are obtained. The cyclotron, although difficult and expensive to construct, has proved to be a powerful and flexible tool for nuclear research.

NUCLEAR BOMBARDMENT REACTIONS

Having described briefly the methods of obtaining the projectiles for nuclear bombardments, we will now present a list of typical reactions. As previously stated, capture of a particle by a nucleus results in an excited compound nucleus which quickly loses its excess energy by a further nuclear reaction. The two steps are illustrated below, with brackets around the compound nucleus.

$$_7N^{14} + {}_0n^1 \rightarrow [{}_7N^{15}]$$

immediately followed by

$$[{}_7N^{15}] \rightarrow {}_6C^{14} + {}_1H^1$$

More frequently the two steps are written as one, without reference to the compound nucleus, thus

$$_7N^{14} + {}_0n^1 \rightarrow {}_6C^{14} + {}_1H^1$$

which may be condensed to

$$_7N^{14}\ (n,p)\ {}_6C^{14}$$

Frequently a variety of reactions is possible with the same projectile. The predominance of a particular one will depend on the energy of the projectile and the nature of the nucleus undergoing bombardment. In the outline of important nuclear reactions below, an attempt has been made to evaluate the various possibilities. The examples given serve to indicate the various reactions possible for a given nucleus and a given particle, and the activity of the product is indicated where it is of value. See later sections for further examples of these reactions and explanations of the decay reactions.

I. *Gamma Reactions:* These high energy radiations are inefficiently absorbed by nuclei, but can cause nuclear transformation.

A. (γ,n): The gamma must have a certain minimum energy for this reaction.

Example 1. $_4Be^9\ (\gamma,n)\ {}_4Be^8$. An important neutron source.

B. (γ,γ): A nucleus can gain energy from gammas and other nuclear particles; paralleled by (p,p), (α,α), (n,n), and (ϵ^-,ϵ^-).

Example 2. $_{49}In^{115}\ (\gamma,\gamma)\ {}_{49}In^{115*}$. Activity: γ, 4.1 hours (isomeric transition).

II. *Proton Reactions:* Coulombic repulsion, which increases with increasing Z, must always be overcome (called capture energy).

A. (p,γ): With protons of capture energy.

Example 3. $_7N^{14}\ (p,\gamma)\ {}_8O^{15}$. Activity: β^+, 126 seconds.

B. (p,α): As type A, but less probable.

Example 4. $_7N^{14}\ (p,\alpha)\ {}_6C^{11}$. Activity: β^+, 20.5 minutes.

C. (p,n): Protons must have somewhat more than the minimum capture energy.

Example 5. $_7N^{14}\ (p,n)\ {}_8O^{14}$. Activity: unknown.

III. *Deuteron Reactions:* Again the coulombic barrier must be overcome (capture energy).

A. (d,p): The coulombic barrier is effectively lowered by "polarization" of the deuteron, in which only the neutron actually enters the nucleus. A very general and useful reaction giving the same end result as (n,γ).

Example 6. $_{17}Cl^{37}\ (d,p)\ {}_{17}Cl^{38}$. Activity: (β^-,γ), 37 minutes.

B. (d,n): Deuterons of capture energy.

Example 7. $_{17}Cl^{37}\ (d,n)\ {}_{18}A^{38}$ (stable).

C. $(d,2n)$: Deuterons must have considerably more than capture energy.

Example 8. $_{17}Cl^{37}\ (d,2n)\ {}_{18}A^{37}$. Activity: ?, 34 days.

D. (d,α): Deuterons of capture energy, but less probable than other low energy processes.

Example 9. $_{17}Cl^{37}\ (d,\alpha)\ {}_{16}S^{35}$. Activity: β^-, 87.1 days.

IV. *Alpha Particle Reactions:* The great coulombic repulsion between this particle and all but the lightest nuclei makes this reaction inefficient.

A. (α,n): Energies somewhat over the capture energy.

Example 10. $_4Be^9\ (\alpha,n)\ {}_6C^{12}$, a useful neutron source.

V. *Neutron Reactions:* Reactions 1 and 10 listed above are frequently used as neutron sources, but the recent development of chain-reacting piles has furnished our best source. The neutron excess of such a device

s enormous by previous standards, and has made possible neutron reactions in macro quantities. Since the neutron is uncharged, the only criteria for its reactions are the energy requirements and the intrinsic probability.

A. (n,γ): With neutrons of vanishingly low energy.

Example 11. $_{37}Rb^{85}$ (n,γ) $_{37}Rb^{86}$. Activity: β^-, 19.5 days.

B. (n,α): With neutrons of vanishingly low energy, but comparatively improbable.

Example 12. $_{37}Rb^{85}$ (n,α) $_{35}Br^{82}$. Activity: (β^-, γ), 34 hours.

C. (n,p): With neutrons of low energy, but widely varying probabilities.

Example 13. $_{37}Rb^{85}$ (n,p) $_{35}Kr^{85}$. Activity: β^-, 4 hours.

D. $(n,2n)$: With high energy neutrons.

Example 14. $_{37}Rb^{85}$ $(n,2n)$ $_{37}Rb^{84}$. Activity: unknown.

E. $(n,$fission$)$: With low energy neutrons on $_{92}U^{235}$, $_{94}Pu^{239}$, and high energy neutrons on $_{92}U^{238}$, $_{90}Th^{232}$. Products: one to three neutrons and a great variety of β^- emitters of $Z = 34$ to $Z = 63$ (*2*, *3*).

NUCLEAR DECAY REACTIONS

Reactions such as those listed in the preceding section form the principal sources of radio-isotopes. The special properties of these isotopes make possible their detection and identification even when present in extremely small amounts. The energy and half-life of a decay reaction are characteristic of the particular nucleus involved, but the decay mechanism and products fall into a few general classifications, which are described below.

Alpha decay consists of the emission from the nucleus of an $_2He^4$ particle. The product nucleus will have an atomic number smaller than that of the original nucleus by two units and a mass number smaller by four units. Alpha particles, because of their charge and mass, have a short but spectacular journey. They produce many ions in a path length of only a few centimeters in air.

Beta decay consists of the ejection by the nucleus of a very energetic electron as a consequence of the transformation of a neutron into a proton. This gives a product nucleus with the same mass number and an atomic number one unit greater. The speedy, light beta particles travel distances up to several meters in air. The amount of ionization per centimeter along their paths is considerably less than that for alpha particles.

Positron decay and *K-capture* produce the same product nucleus. In each case the atomic number of the nucleus decreases by one unit and the mass number remains the same. A positron is a positive electron and its characteristics are those of a beta particle except for the difference in charge. The alternate process is that an extra-nuclear electron, as of the *K*-shell, may be captured by the nucleus. The outward manifestation of this decay is the emission of X-rays as the hole in the electronic shells is filled.

Isomeric transition is the loss of energy by a nucleus with no change in atomic or mass numbers. The energy may be lost as a gamma ray or by giving the energy to an extra-nuclear electron. In this latter case, low energy electrons and X-rays are observed.

Neutron decay is observed in a few of the very unstable products of nuclear fission. The Smyth report (*3*) lists the half-lives of four such isotopes. Chemical identification is difficult.

DETECTION AND MEASURING DEVICES

The detection and measurement of nuclear decay products depends, directly or indirectly, on the ionization which they produce; therefore, the efficiency of any such device in general will be proportional to the ionizing ability of the particular radiation being observed. In contrast to alpha and beta particles the electrical neutrality of neutrons makes them very inefficient ionizers. Only secondary particles, resulting from collision or capture, are ordinarily observed. Gamma and X-radiations produce ions only on absorption, and they are very poorly absorbed due to their great energy.

Direct recognition of the ionizing properties of a given radiation is possible by means of the Wilson *cloud chamber*. In this device the ions formed by the radiation serve as nuclei for the condensation of visible droplets of water from an atmosphere which is supersaturated with water vapor. Tracks of alpha particles are readily seen, beta particles less easily, and neutrons and gamma rays not directly at all. Absorption or collision of these last two types produces secondary particles which can be detected.

Electroscopes and *electrometers* in many forms are used to detect ionization accompanying radioactive decay. In their general form they simply measure the loss in charge from an insulated plate when the surrounding gas is ionized by the radiations. Alpha particles, because of their heavy ionization, can be detected almost individually, while several thousand beta particles or several hundred thousand gamma quanta are needed to produce a detectable effect.

In an *ionization chamber* the ions formed by the radiations give rise to a flow of current between two electrodes maintained at different potentials. This minute current can be amplified electronically to give a quantitative measure of the activity present. Again the smallest detectable amounts of radiation increase rapidly from alphas to betas to gammas, due to their difference in ionizing ability. A special adaptation of this device utilizing the nuclear reaction

$$_5B^{10} + {}_0n^1 \rightarrow 2\,{}_2He^4 + {}_1H^3$$

is used to detect neutrons. The above reaction is quite efficient and the ionization due to the secondary alpha particles is readily measured.

Since single beta particles and gamma quanta do not in themselves produce enough ionization to be directly detectable, a device known as a *Geiger-Müller counter* is commonly used when limited amounts of activity are present. It consists of a central wire held at several

hundred volts positive potential with respect to a surrounding cylindrical shell. With the proper mixture and pressure of gases (frequently 8 cm. of argon plus 2 cm. of alcohol vapor) this device will detect single betas and gammas. The potential is adjusted to a point slightly below the value where spontaneous discharge takes place. In this condition the passage of a single ionizing particle through the field is sufficient to cause a discharge and a flow of a current many magnitudes greater than that due to the particle itself. Gamma quanta are not counted directly by such a device, but the electrons they eject on being absorbed in nearby matter will trip the counter. Their low absorption coefficient makes this process about one-hundredths as efficient as beta counting.

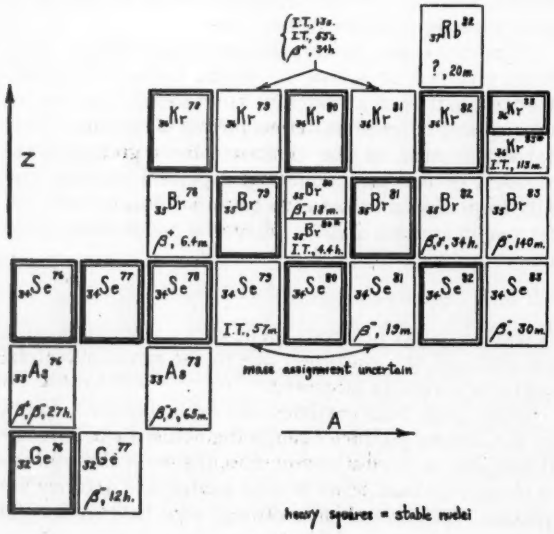
THE ISOTOPE CHART

The method of summarizing information about the relationships of the stable and radioactive nuclei illustrated in the figure will serve to present a few practical illustrations of the principles outlined above.

As might be expected, the radioactive nuclei with a higher atomic number than their stable isobars will show β^+ activity, and those with lower atomic numbers, β^- activity. A chain of several decays may take place until the stable isobar is reached as in the case of mass number 83 in the figure.

Alternate paths of decay are occasionally observed, as in the case of 27-hour $_{33}As^{76}$. This nucleus emits both positive and negative beta particles, decaying to either of its stable isobars, $_{32}Ge^{76}$ or $_{34}Se^{76}$. This possibility is always present when a radioactive nucleus is flanked by two stable isobars, but usually one mechanism is predominant over the other, as in the case of 6.4-minute $_{35}Br^{78}$ and 34-hour $_{35}Br^{82}$.

Isomeric transition is a fairly common type of decay, although often hard to recognize. It occurs in both stable and unstable nuclei. $_{36}Kr^{83}$ is a stable, naturally occurring nucleus, having an excited state which is produced when $_{35}Br^{83}$ emits a beta particle. On the other hand, when $_{35}Br^{80}$ is formed by an (n,γ) reaction on $_{35}Br^{79}$, an excited isomer results. The decay of $_{35}Br^{80*}$ isomer with a 4.4-hour half-life is followed by beta emission of the lower state $_{35}Br^{80}$ with 18-minute half-life to form stable $_{36}Kr^{80}$.



Several krypton activities (13 seconds, 55 seconds, 34 hours) are formed by (p,n) reaction on bromine. They cannot be assigned definite mass numbers because they could be products of either of the two stable isotopes of bromine. This same uncertainty exists with the selenium activities formed by (n,p) on bromine. Two bromine activities are also produced by (n,γ) on bromine, but a similar confusion is avoided by use of additional nuclear reactions. The 34-hour bromine is also formed by (n,α) on rubidium, and the lightest stable isotope of this element is $_{37}Rb^{85}$. Also, the 4.4-hour bromine is produced by $(n,2n)$ on bromine. These two reactions make it apparent that 4.4-hour bromine must have mass number 80 and 34-hour bromine must have mass number 82.

As a final illustration, let us consider the various activities which can be produced by bombardment of a single nucleus, say $_{35}Br^{79}$. Gamma rays of high energy will produce, by (γ,n) reaction, 6.4-minute $_{35}Br^{78}$. As stated above, the (p,n) reaction may give one of several krypton activities. (p,γ) and (p,α) reactions will produce the stable nuclei $_{36}Kr^{80}$ and $_{34}Se^{78}$. Deuteron bombardment will give, by (d,p) reaction, 4.4-hour $_{35}Br^{80*}$ and the 18-minute $_{35}Br^{80}$. At high deuteron energies the $(d,2n)$ reaction will produce the krypton isotope obtained by (p,n) reaction. The (d,n) and (d,α) reactions will produce the stable isotopes $_{36}Kr^{80}$ and $_{34}Se^{77}$. The (α,n) reaction will give 20-minute $_{37}Rb^{82}$. Neutrons will produce a variety of activities. With low energy neutrons the principal reaction will be (n,γ) to give 4.4-hour $_{35}Br^{80*}$ and 18-minute $_{35}Br^{80}$. A small amount of 27-hour $_{33}As^{76}$ may also be produced by the (n,α) reaction. At higher neutron energies the (n,p) and $(n,2n)$ reactions will become important, giving $_{34}Se^{79}$ and 6.4-minute $_{35}Br^{78}$.

This article will have served its purpose if it has given the reader a nodding acquaintance with the language and techniques of nuclear reactions. For a more detailed account, yet still not highly specialized, the book by Pollard and Davidson (*4*) is recommended. A rather complete table of the properties and reactions of stable and radioactive isotopes compiled by Seaborg is also available (*5*).

ACKNOWLEDGMENT

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Methods of Separation and Tests for Purity

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ONE of the major problems of chemistry, one which faces almost every active chemist, is that of separation and purification. The problem arises in analytical work of any kind, and it shows itself also in synthetic chemistry during the preparation of starting materials and the working up of final products. Separation and purification are the same in principle; they involve the sorting out or apart of molecules from mixtures. The problem is called one of separation when the proportions of the various molecules in the mixture are not too disparate, and it is called purification when the molecules of one kind are present in the greatest proportion and those of the other kind or kinds (the impurities) are present in relatively small amount. Since the same principle underlies separation and purification, the methods used to accomplish them will be essentially the same.

The number of separation processes which exist is so great that the only practical course in a paper like this is to select a few for discussion. In this paper, therefore, only those in most common use will be dealt with, but the method of treatment of them will suggest its application to some other separation processes. The object of this paper will be to show the relations between four separation processes, the differences between them, and the principles upon which they operate. Distillation, crystallization, solvent partition, and adsorption processes will be discussed. A further object of this paper will be to discuss tests of purity, since these involve the use of separation processes, and to show the principle which underlies the most reliable type of test of purity.

What one tries to do in the separation processes is to sort molecules. The better the process, the more efficient the sorting is and the more clean the separation achieved. However, we cannot pick out molecules individually the way we might sort a deck of cards. (It would be an endless job, for one thing, but under certain circumstances it would be a most useful accomplishment. No one has yet contrived an inexpensive way to do it.) What we actually do is to provide an environment such that the molecules can become sorted under some driving force, and then we give sufficient time for this to be accomplished. The sorting processes which the molecules undergo under suitable conditions are known as partition or distribution processes and underlie all the separation processes treated in this paper. The partition or distribution occurs when the molecules are placed in an environment such that they can lose energy of some kind by undergoing the partition, which then occurs spontaneously.

Distillation, crystallization, solvent partition, and adsorption all involve partition, but the environment in which the partition occurs is in each case different. Different, also, are the mechanical aspects of the separation, for the separation process ends up eventually as a mechanical operation. What is done is to provide an environment suitable for the partition and then, after the molecules have sorted themselves, to complete the separation by mechanical means.

Consider, for example, a distilling flask containing a mixture of a low-boiling substance, B, and a high-boiling one, A, part of the flask being filled with liquid, and the region above it with vapor in equilibrium with the liquid (Figure 1). We have in the flask two phases—a liquid phase and a vapor phase. (A phase is a homogeneous body which can be separated mechanically from neighboring phases. The glass of the flask is a phase, but we can neglect it here since it is not appreciably involved in this partition. Also, we can neglect the cork phase and any air which may be present.) The molecules of A and B will be present in both phases. B is more volatile than A, and there will be a greater tendency for B molecules to go into the vapor phase than for A molecules, and conversely A will have a greater tendency than B to remain in the liquid. It is evident, therefore, that here already is a partition. If we wished, we could draw off the liquid into a fresh flask and let vapor form above it, giving time for equili-

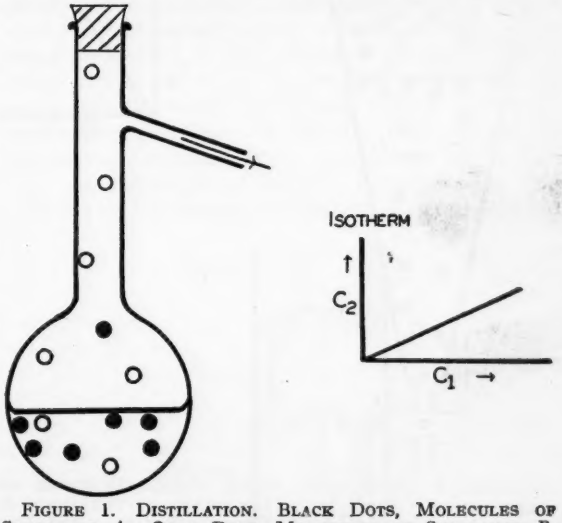

FIGURE 1. DISTILLATION. BLACK DOTS, MOLECULES OF SUBSTANCE *A*; OPEN DOTS, MOLECULES OF SUBSTANCE *B*. THE SIDE-ARM OF THE FLASK MAY LEAD TO A CONDENSER.
System: distribution between liquid and vapor phases
Relation: $C_1 = KC_2$ (dilute solution), where C_1 = concentration of A molecules in liquid, and C_2 = concentration of A in vapor at equilibrium; K is a constant
Separation process: distillation
Countercurrent application: fractional distillation with reflux

brium to be approached. Again we get more *B* than *A* molecules in the vapor. We could again draw off the liquid, let vapor form above it, and repeat the process until eventually relatively few *B* molecules would be left in the liquid. This would be tedious and is not generally the useful procedure, but it would give a separation of *A* from *B*. In practice it is much more convenient to change the environment of the system so as to make the process more rapid and the separation of the phases easier. This is done by heating the mixture, which causes the vapor pressures of both *A* and *B* to increase. The relative discrepancy between numbers of *A* and *B* molecules in the vapor still remains, so that as the vapor is formed and driven off from the liquid by the heating, relatively more *B* than *A* molecules are lost from the liquid. The vapor can be collected by condensing it, when one will obtain, at least at first, a liquid relatively richer in *B* than *A*. In this operation one has allowed molecules of *A* and *B* to sort themselves (on the basis of their physical properties) by supplying favorable conditions for partition (*i. e.*, an increased temperature to favor partition into the vapor phase) and then one has completed the separation by mechanical means (separating and condensing the vapor phase).

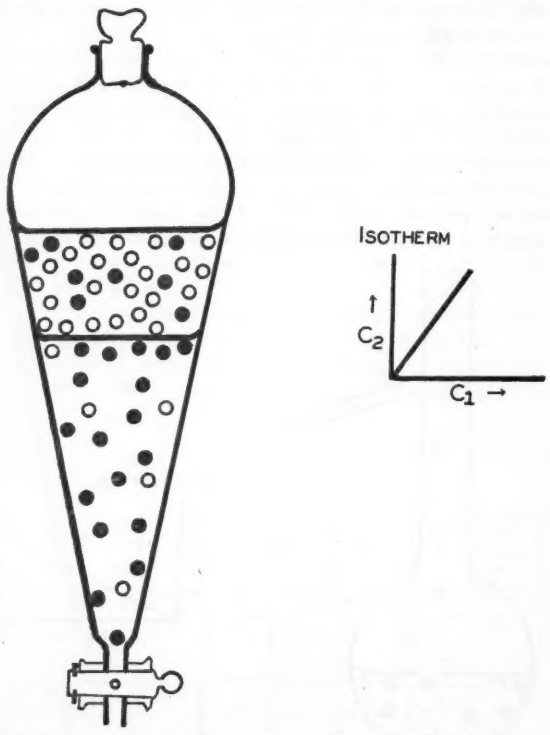

FIGURE 2. EXTRACTION. BLACK DOTS, MOLECULES OF SUBSTANCE *A*; OPEN DOTS, MOLECULES OF SUBSTANCE *B*. THESE ARE DISTRIBUTED IN DIFFERENT RATIOS IN THE TWO LIQUID LAYERS IN THE SEPARATORY FUNNEL.

System: distribution between two liqui l phases

Relation: $C_1 = kC_2$ (ideal case), where C_1 = concentration of *A* molecules in lower liquid phase, and C_2 = concentration of *A* molecules in upper liquid phase at equilibrium; **k** is a constant

Separation process: liquid-liquid extraction

Countercurrent application: countercurrent extraction, "partition chromatography"

The partition relation can be stated in symbols. In a dilute solution at a given temperature the concentration of the *B* molecules in the vapor phase (C_{vapor}) bears a constant relation to the concentration of the *B* molecules in the liquid phase (C_{liquid}); thus, $C_{vapor} = KC_{liquid}$, and if *C* is measured in terms of the fraction of all the molecules present (mol fraction) then *A* molecules are simply accounted for too. Of course there are many special cases and deviations from the simple relation given above, but the principle involved in the separation holds.

In crystallization the partition is between a solution and a solid. Here the environment, the solvent and temperature, is chosen so that, say, molecules of *A* remain in solution while molecules of *B* tend to crystallize. This is accomplished by choosing a solvent in which *A* is more soluble than *B*. All of the mixture of *A* and *B* is first dissolved, then the temperature is lowered to a point at which *B* crystallizes but at which the solution is not yet saturated with *A* so that *A* does not tend to come out. (When *B* crystallizes, some *A* is almost always brought down, either through weak attractive forces between *A* and *B* molecules or by inclusion with solvent in imperfections in the crystals of *B* or through other causes such as the formation of solid solutions. The sorting is therefore again not perfect.) Time is then allowed for the crystallization of *B* to go as far as it will. The mechanical part of the separation process comes when the two phases are separated; the solid is filtered or centrifuged from the liquid. The separation can be improved by repeating the operation on the two fractions obtained.

The equation which can be written here is like that for distillation; the concentration of *B* molecules in the saturated solution at a given temperature is equal to a constant multiplied by the concentration in the solid. But the effective concentration in the solid is practically constant, so that in effect $C_{solution} = \mathbf{K}$. This is the familiar statement of conditions in a saturated solution in equilibrium with the solid substance at a given temperature.

In liquid-liquid partitions the distribution is between two liquid phases. Here the environment of solvents and temperature operates in this way: *A* and *B* molecules mixed together in a given solvent, say water, are shaken together with some other solvent which is nearly immiscible with the water, say ether, and then the mixture is allowed to separate into two liquid phases. If the two solvents are carefully chosen, then it will be so that the molecules of one of the substances, for example *A* molecules, have a relatively greater tendency to remain in one phase than to go into the other, whereas those of *B* show the opposite tendency (see Figure 2). Thus *A* may be more soluble in water than in ether while *B* is more soluble in ether than in water. One need now only separate the layers mechanically (with a separatory funnel) in order to have a partial separation of the molecules. The separation will not be a perfect one with all *A* mole-

cules in one phase and all B in the other, but it can represent a good sorting of the original mixture, and, of course, it can be repeated with the two separate fractions. The separated substances A and B can be recovered by evaporating or otherwise removing the respective solvents. This is also a separation process, but it can be made easy by the choice of solvents if one looks ahead to it.

The partition here can be stated in the ideal case thus: the concentration of A molecules in the water phase bears, at a given temperature, a constant relation to the concentration of A molecules in the ether layer, or $C_{water} = kC_{ether}$. The relationship, with a different k, holds also for B molecules. This statement looks like the other ones given above and so emphasizes the similarity of the processes involved.

In adsorption separations the partition is between a solution (or gas) and a surface (interfacial) phase. Adsorption is a phenomenon in which a substance becomes concentrated at a surface. The suitable environment here necessitates the choice of an appropriate temperature and solvent and the obtaining of a large surface area. This last requirement is met by using finely powdered adsorbents which have very great surface areas per unit of mass. The great surface area is obtained not only by powdering the substance (the smaller a particle the greater its area for a given mass) but also by making it porous. Charcoals and certain clays are adsorbents of this kind. However, it is not sufficient merely to obtain a large surface. The nature of the surface plays an important role. A surface should be chosen so that when it is put in the solvent which is to be used, the interface, or surface phase, formed adsorbs one type of molecule, say A, more than the others. When this is achieved and the adsorbent is shaken with the solution, then the partition which occurs leads to a separation. This is because relatively more of the A molecules move into the interface than of the others (B) and then the solid adsorbent including the interface can be removed mechanically by filtration or centrifugation from the liquid phase (Figure 3). The adsorbed molecules can be desorbed with a suitable solvent and thus recovered. The partition is, again, hardly ever perfect. Some A molecules remain in solution and some B are absorbed, but the operation may be repeated on the two fractions to improve the separation.

The partition relation here needs several constants to describe it. In a simple case it is found that concentration of molecules of A in the interface ($C_{interfacial}$) bears a constant relation to some power (n) of the concentration of A molecules in the solution at equilibrium at a given temperature; thus, $C_{interfacial} = \mathbf{k}(C_{solution})^n$. It can be seen at once that if n were equal to 1, then this equation would be identical with the others in form. As with the other partitions more complicated cases occur, and special equations are needed to describe these.

A very important conclusion which one must reach from the descriptions given above is that a single partition operation almost never gives a completely pure substance. Whatever the system of phases involved, there are almost always bound to be molecules of each component in each phase. This would seem to indicate that it would be very difficult to get a *complete* separation. However, one could always improve the degree of sorting by subjecting each fraction to another partition. The main point is that in actual practice one would not expect ever to get a complete separation and hence a completely, *absolutely* pure substance. One only expects a sufficiently pure substance (see below). When the requirements for purity are not very high, then a single partition may give all the purification desired. Usually, though, it is found that single partitions are not sufficient, and the repetition of the separation process is then necessary. This is often found to be the case when chemically closely-related substances are being separated. Under circumstances such as these many repetitions of the separation process may be needed and this would become quite tedious. However, such tedious repetition can often be evaded by the application of a principle, at times designated as the principle of countercurrent action. Application of this principle leads to a sort of mechanical integration of the

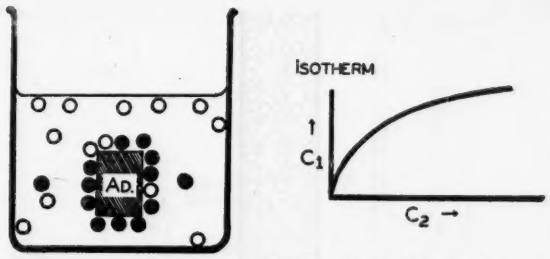

FIGURE 3. ADSORPTION. BLACK DOTS, MOLECULES OF SUBSTANCE *A*; OPEN DOTS, MOLECULES OF SUBSTANCE *B*. AD. = ADSORBENT.
System: distribution between liquid and interfacial phases
Relation: $C_1 = \mathbf{k}C_2^n$, where C = concentration of A molecules in the interface and C_2 = concentration of A molecules in the solution at equilibrium; $\mathbf{k}$ and n are constants
Separation process: simple adsorption, decolorization
Countercurrent application: chromatographic adsorption analysis

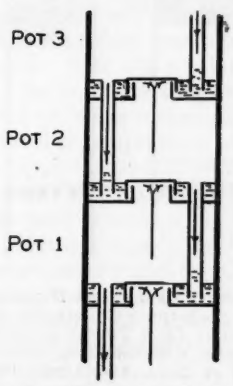

FIGURE 4. BUBBLE-CAP DISTILLING COLUMN, SHOWING PART OF THE COLUMN. ↑ PATH OF THE RISING VAPOR; ↓ PATH OF THE DESCENDING LIQUID.

FIGURE 5. PACKED DISTILLING COLUMN, SHOWING PART OF THE COLUMN. THE TORTUOUS PATHS OF RISING VAPOR AND DESCENDING LIQUID MAY BE IMAGINED. THE COLUMN IS PACKED WITH INERT MATERIAL.

many repeated steps so that efficient separations may be obtained relatively easily.

The application of this principle to distillation may be made in several ways. One method is to arrange a series of distilling pots one on top of the other and all connected so that vapor from a lower one can flow into the next higher one, and liquid from that one can overflow to the one below (see Figure 4). Above the boiling liquid in a pot, the more volatile substance distributes itself into the vapor phase in higher ratio than the less volatile. This vapor passes up from, say, pot 1 into pot 2, bubbling through a layer of liquid in pot 2. This liquid, which is boiling at a slightly lower temperature than that in pot 1 (because its composition is different and it contains relatively more of the volatile component), condenses out some of the vapor, but relatively more of the high-boiling molecules are condensed than

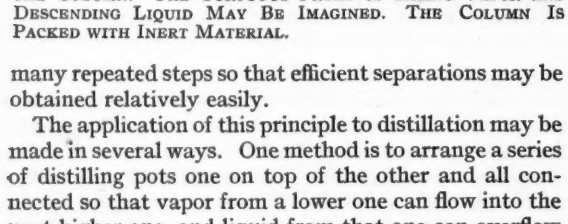

FIGURE 6. CHROMATOGRAPHY OF A MIXTURE OF TWO SOLUTES *A* AND *B*. *a*, THE SOLUTION *S* CONTAINING *A* AND *B* IS PLACED ABOVE THE ADSORBENT *Ad*; *b*, THE SOLUTION HAS BEEN PRESSED INTO THE ADSORBENT, A MIXED ZONE *AB* IS FORMED, AND THE LIQUID LEVEL IS AT *L*; *c*, DEVELOPER LIQUID *D* IS BEING PASSED INTO THE COLUMN AND DEVELOPMENT OF THE ZONES IS BEGINNING; *d*, CONTINUED PASSAGE OF DEVELOPER LIQUID HAS PRODUCED A DEVELOPED CHROMATOGRAM, WITH THE SEPARATE ZONES SHOWN AT *A* AND *B*.

of the more volatile ones so that in pot 2 the less volatile molecules are partially scrubbed out of the vapor from pot 1. This vapor from pot 2 then passes to pot 3 where through a similar process it becomes relatively richer in more volatile molecules. If vapor is continuously supplied to pot 1, then partial condensation in this pot allows liquid to overflow the trap and trickle down to the pot below; similarly there is overflow of liquid enriched in less volatile molecules from pots 2 and 3. It can be seen, therefore, that the liquid moves downward, and vapor upward, *i. e.*, the two move counter to each other, the liquid washing from the vapor less volatile (more condensable) molecules, and the vapor stripping the liquid of the more volatile molecules. Each pot is a little still. The efficiency of the process increases primarily with the closeness to which equilibrium is approached in each pot. Many industrial fractionating stills are of this type.

Another method of obtaining countercurrent distillation is to allow vapor to pass up a tube and to condense some of it near the top of the tube and let it run back. The tube is usually packed with some inert material which fills much of it and forces the vapor to follow a tortuous path up the tube; the returning liquid which flows over the packing thus has good opportunity to come into contact with the vapor so that partition can occur as explained above. This apparatus is a packed distilling column and may be a very efficient countercurrent device (Figure 5). Stills of this type are also much used in industry.

The countercurrent principle can be applied to other partitions. Liquid-liquid extractions may be carried out this way, and many machines have been devised for this purpose. One may, for example, use a tower similar to a distilling tower and allow a heavy liquid to trickle downward over the packing while a less dense one rises upward countercurrently to it. The sorting-out process occurs across the areas of contact of the moving liquids. One may set up a row of separatory funnels which are used in succession, or these may be embodied in a machine, as Craig (*1*) has done. In one ingenious arrangement one of the liquids is fixed by adsorption to a finely divided solid and the other liquid is allowed to percolate downward through the fixed mass (*2*).

Adsorption may be applied countercurrently, either by the use of a number of coupled stages (analogous to the set of distilling flasks or the set of separatory funnels) or else by the use of a Tswett chromatographic column (*3*) (Figure 6). In this latter procedure the adsorbent is placed in a tube and the fluid which serves as the second phase is passed upward or downward through the column of adsorbent, *i. e.*, countercurrently to it. Here the more strongly adsorbed molecules (*A*), being held most tightly in the interface, congregate near where the fluid enters the adsorbent. The less tightly held ones (*B*), the available interface being first filled up chiefly with *A* molecules, move further on along the column where they may be adsorbed. Then if one passes pure solvent through the column, one can wash

B molecules along the adsorbent farther and farther from the *A*, which are washed along the adsorbent with greater difficulty. This may lead, eventually, to complete separation of the molecules. The column of adsorbent may then be extruded from the tube and cut between the zones of adsorbed *A* and *B* molecules. These can then be desorbed from the separated sections of column and recovered.

The countercurrent principle has been applied to crystallization (*4*), but it appears that no one has contrived a machine for it comparable in simplicity to those available for the other separation processes.

The theory of the different separation methods may be found in some of the references given above. It cannot be taken up here. In some cases it is exceedingly complicated and incompletely worked out.

It was stated above that it is unlikely that any substance can be prepared in quantity absolutely free from foreign molecules. Furthermore, if one foreign molecule were present in a small amount of the substance, it would not be possible to detect it, except in the rarest cases; therefore, the definition of a pure substance would not be useful if it meant a substance with no foreign molecules in it. The criterion of purity to be useful must rest upon experimental operations, and the best definition might be that a *substance can be called pure when it cannot be proved impure.* Thus, if the test for impurity which is used is a crude one, then the substance which passes the test is at least as pure as the crude test indicates. If a substance passes tests which are extraordinarily penetrating, then that substance is extraordinarily pure. Purity is a relative matter (*5*).

Tests of purity are many in number, and those which are the most penetrating have this characteristic in common: *they combine an attempt at separation with a method of comparison of the separated fractions.* The discussion of tests of purity fits in, then, with the discussion of separation methods, and each of the four separation methods dealt with above has its characteristic application in testing for purity. The test is often not carried out in its most penetrating form. To give the tests maximum acuity, it is necessary to invoke the principle enunciated above, to combine separation and comparison. This may be done, often with relatively simple apparatus, in the ways described below.

If the separation process involves distillation, then one employs an ebulliometer (*6*), a device (Figure 7) by means of which the boiling *temperature* of a liquid may be compared with the condensing *temperature* of its vapor. If these are the same (within the limits of measurement used), then the substance is behaving like a pure substance (within the limits of the test). Certain complications (the existence of azeotropic mixtures) make it so that the test becomes more acute if the measurements at one pressure are compared with those at another, for then an additional factor which would show up the presence of impurity is introduced—namely, the pressure change which affects the sorting process of different molecules differently. The test

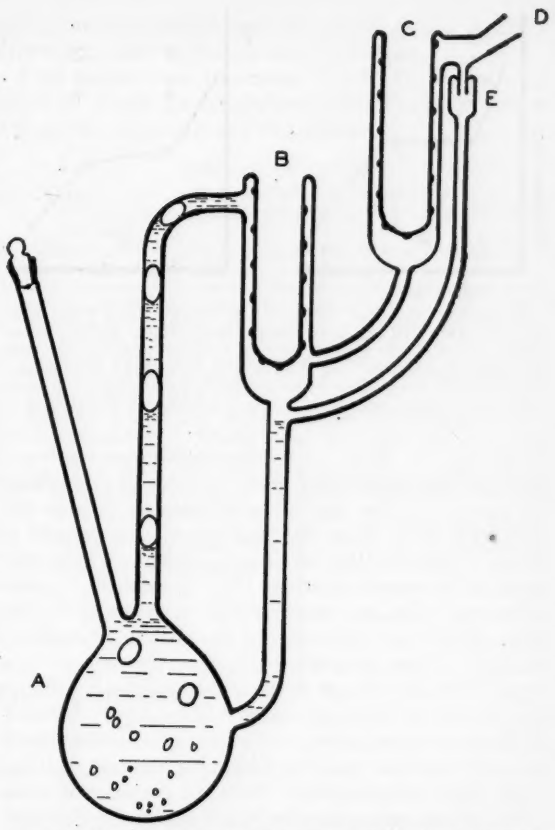

FIGURE 7. DIFFERENTIAL EBULLIOMETER, AFTER SWIETOSLAWSKI. THE LIQUID BOILING IN *A* IS LIFTED BY ITS OWN VAPOR AND THROWN ON TO THE THERMOMETER WELL *B* WHERE THE TEMPERATURE OF THE BOILING LIQUID MAY BE MEASURED. VAPORS PASS ON TO THE WELL *C* WHERE THE TEMPERATURE OF THE CONDENSING VAPOR MAY BE MEASURED. A CONDENSER AT *D* RETURNS LIQUID THROUGH *E*, WHERE THE DROP-RATE MAY BE MEASURED.

relies upon the fact that impurity will be concentrated either in the vapor or the liquid and be shown up in the comparison of the two temperatures measured for the boiling liquid and the condensing fractionated vapor.

If the separation process involves crystallization, then the test of purity which uses it employs a cooling (or heating) curve. Here the substance is allowed to cool slowly from the liquid state past the freezing point to the solid state while the temperature is read at recorded intervals. The temperature read when freezing just starts is compared with that obtained when freezing is almost over. If the two temperatures are the same (within the limit of accuracy of the thermometer used), then the substance is pure (to the extent implied by the temperature measurement). Certain complications (supercooling, formation of eutectics) may affect the measurement and make interpretation difficult. The test is visualized by recording temperature against time (Figure 8). At the transition point there is a "hold" at which the slope of the cooling curve changes. In the ideal case (no impurity) the curve becomes quite

FIGURE 8. COOLING CURVES. *A*, CURVE OF A PURE SUBSTANCE; THE DOTTED LINE SHOWS THE EFFECT PRODUCED BY SUPERCOOLING. *B*, CURVE OF AN IMPURE SUBSTANCE; THE DOTTED LINE SHOWS THE CURVE FOR THE PURE SUBSTANCE; THE ARROWS INDICATE, 1, BEGINNING OF FREEZING, 2, END OF PROCESS, WHICH MAY BE SOMEWHAT INDEFINITE IN CASE *B*.

flat during the "hold," indicating that during the freezing time the temperature does not change, remaining the same from the beginning of freezing to near the end of freezing. Such an ideal situation is difficult to realize experimentally for many reasons. These may be found discussed elsewhere (*7*). If impurity is present in the substance being tested, it shows up in this way: the major component of the mixture crystallizes out more or less pure while the impurity remains to a large extent in solution in the still liquid part. But as the amount of liquid decreases due to the crystallizing of the major component, the relative concentration of impurity increases and the remaining solution of it becomes more concentrated. Now the presence of a dissolved second substance almost always lowers the freezing point of the first one, the degree of lowering depending upon the concentration of solute present. Hence as the freezing continues and the relative concentration of impurity increases in the unfrozen part, the freezing point drops more and more; thus, instead of the horizontal "hold" obtained for the pure substance there is found a "hold" with a sloping curve. The initial amount of impurity present may often be estimated from the shape of the curve.

Both this test of purity and the previous one have this in common—that they allow a separation process to occur in the neighborhood of a transition point (freezing point, boiling point) and compare the compositions of the phases by means of their temperatures of transition.

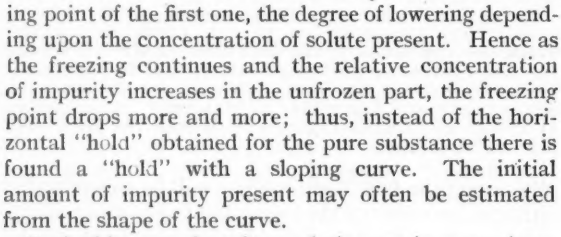

FIGURE 9. DISTRIBUTION CURVES, AFTER CRAIG. *N*, NUMBER OF THE EXTRACTION CHAMBER. THE TOTAL CONCENTRATION OF SOLUTE IN THE GIVEN CHAMBER IS PLOTTED ON *C*. THE DOTTED LINE REPRESENTS THE DISTRIBUTION CURVE OF A PURE SUBSTANCE; THE SOLID LINE REPRESENTS THE DISTRIBUTION CURVE OF A MIXTURE OF TWO SUBSTANCES, AND TWO PEAKS REPRESENTING THE SUBSTANCES ARE SEEN IN A STATE OF PARTIAL SEPARATION.

If the separation process is that of liquid-liquid partition and if the substance is pure, its *composition* in each liquid phase should be the same although its concentration may be different—that is to say, if the partition is carried out and the solvent is removed from each fraction, then the products obtained should be identical. This test is made most conveniently by Craig's countercurrent analytical method (*1*) or by Martin and Synge's "partition chromatogram" (*2*). In the former method a machine consisting of a number of separatory chambers is used. This machine (a set of separatory funnels could be substituted) makes it possible to bring the one phase from a separation into contact with a succession of portions of the other phase so that a large number of partitions can be carried out in a countercurrent manner. The chambers are examined after a given number of partitions have been carried out, and the concentration of substance in each is plotted against the number of that separatory chamber. By this device of plotting Craig obtains the distribution curve of substance throughout the system of separatory chambers, and if the substance is pure, this curve is symmetrical, provided the isotherm is linear (Figure 9, dotted line). If impurity is present, the curve shows humps or bulges in the main curve which indicate the quantity of impurity and suggest that if the partition process had been continued, the impurity would have separated out with a separate distribution curve of its own (Figure 9, solid line).

In Martin and Synge's method the one phase is held fixed by adsorption to a solid. This is supported in a tube and the other phase is allowed to trickle down over it. Partition occurs with the formation of a zone much as in the case of chromatography (Figure 6). If impurity is present, it may appear at the leading or at the following edge of the main zone of substance and either migrate away or be left behind as a separate zone (as in Figure 6*c* and 6*d*). The details of both these methods are to be sought in the original papers.

When adsorption is employed as the separation process, then the test of purity comes in an attempt to separate the substance chromatographically. Here impurity usually shows a degree of adsorbability which is different from that of the substance under test; hence, it will form a zone on the Tswett column (Figure 6*c*) which will move at a different rate from the zone of the major component of the mixture. This zone will either be left behind, if it is more strongly adsorbed than is that of the major component, or else it will migrate away from the other if it is less well adsorbed. In any case, the appearance of more than a single zone indicates that a separation has occurred in which the two fractions are not identical and hence that the original substance applied to the column was not pure (unless it was altered by the adsorbent).

The ideas presented in this essay may be summarized as follows. Separation of mixtures is a fundamental

problem which confronts chemists. A number of diverse operations and processes are seen to rest upon common principles. The most common separation processes involve two operations: the setting up of a suitable environment so that the molecules of the mixture may distribute themselves between two or more phases, and the mechanical separation of the phases after the distribution has been allowed to proceed sufficiently far. These operations may be carried out in two ways, either in single batch-wise steps or in a countercurrent manner. The latter is shown to have distinct advantages over the former.

Purification is a special case of separation in which one of the components of the mixture is present in very large ratio to the others. Tests of purity depend on the use of separation processes, and the most penetrating tests of purity combine a separation process with a method of testing the fractions obtained. Identity of the fractions after attempts at separation is a test of purity. The degree of purity of a substance which passes the tests is no greater than the ability of the separation method to discriminate between the substance and impurities and the acuity of the tests of identity applied to the separated fractions.

I am indebted to Professors Harold G. Dietrichand Scott E. Wood for helpful suggestions and criticisms during the preparation of this paper.

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Teaching Total Acidity

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TOTAL acidity is measured by the titration of an acid with a base or vice versa. In titrating a base with an acid of known concentration, the strength of base is determined. The following plan for teaching the mathematical aspects is followed in the general chemistry course.

A buret is filled with previously standardized hydrochloric acid. A second buret is filled with the base, sodium hydroxide, whose strength or normality is being determined. Twenty-five milliliters of acid are carefully run into a beaker and three drops of phenolphthalein are added. The sodium hydroxide is carefully added to the beaker of acid with constant stirring until the end point of faint pink coloration is reached. No attempt is made to eliminate the possibility of carbon dioxide from the air settling in the beaker and thereby fading the end point of the indicator.

In this experiment no mention is made of the term "normality" until the experiment is completed. The volumes of acid and base are written on the blackboard as follows:

Volume of HCl: 25.00 ml.
Volume of NaOH: 38.00 ml.

Ask the class the following questions:

(1) What conclusion would you draw if we used identical volumes?

(2) What volume relations exist in this experiment?

(3) How would you express this answer in terms of strength of acid and base? (Acid is stronger than base. Base is weaker than acid.)

(4) Since the base is weaker than the acid, how may the strength of base be quantitatively expressed?

The base is 25/38ths as strong as the acid. Expressed decimally, it is the ratio 0.657/1. Taking the strength of acid as 1, then the strength of base is 0.657. If the acid strength is called 1 Normal, then the base is 0.657 Normal. If the strength of acid of this experiment is 0.1 *N*, then the strength or normality of the base is 0.0657.

Expressed as a ratio, it is:

$$25{:}38 \; :: \; x{:}\; 0.1$$

Expressed as a general formula it is:

$$\text{ml.} \times \text{normality (base)} = \text{ml.} \times \text{normality (acid)}$$

The definition of normality may now be given as the weight of a gram equivalent of a substance dissolved in a liter of solution.

$$\text{Normality} = \text{number of gram equivalents/volume in liters}$$

Conclusions: (1) The term "normality" is determined experimentally by treating the term as strength. (2) No formula memorization is tolerated without rational justification.

Rearrangement of Substituted Benzopinacols

Application of Electronic Theories

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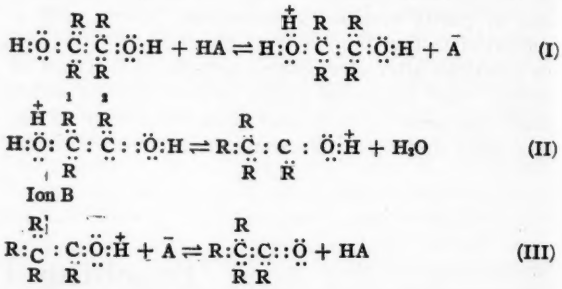
ONE of the more popular experimental approaches to the nature of the pinacol-pinacolone rearrangement has been that of determining the relative "migration aptitudes" (*4, 23*) of various groups. These have usually been expressed as a ratio of the amounts of R′R′ØCCOØ (R′ migration) to ØØR′CCOR′ (Ø migration) formed by the rearrangement of symmetrical pinacols of the type ØR′C(OH)C(OH)R′Ø, the phenyl group being used as a standard. In 1932 W. Bachmann (*2*) and his coworkers began a careful study of the rearrangement products obtained from such pairs of isomeric substituted benzopinacols as R′RC(OH)C(OH)RR′ (I) and RRC(OH)C(OH)R′R′ (II). Their results were surprising in that the order of the migration aptitudes obtained from an analysis of the products from symmetrical pinacols (I) was usually exactly the reverse of that revealed by similar data for the corresponding unsymmetrical pinacols (II). It is the purpose of this discussion to review the present status of the facts and hypotheses concerning the rearrangements of substituted benzopinacols and to describe a qualitative correlation which appears to exist between migration aptitudes and experimentally determined relative electron densities.

Three items concerning the existing experimental data are worth noting. The first concerns the small number and variety of radicals which are found in the benzopinacols mentioned in the literature. The migration aptitudes of only about 15 substituted phenyl groups have been reported, and these fall into only three classes: seven are completely hydrocarbon, five have halogen substituents, and three have ether substituents. The second is the fact that in practically all pinacol-pinacolone rearrangements all radicals present migrate to some extent, and the final product is therefore determined by the relative rates of migration. The third is the observation by Hatt, Pilgrim, and Stephenson (*17*) that the same value for the migration aptitude of the *p*-biphenylyl radical is obtained when s.-di-*p*-phenylbenzopinacol is caused to rearrange in the presence of any one of three acid catalysts, but that quite a different value results when a fourth catalyst, acetyl chloride in benzene-acetic acid, is used. Unfortunately, many of the quantitative data of Bachmann (*2, 3, 4, 5, 6*) were obtained using this catalyst. These observations of Hatt, Pilgrim, and Stephenson would therefore appear to negate some of the quantitative data appearing in the literature, although qualitative conclusions regarding the relative order of migration aptitudes may not be seriously affected. This point remains unsettled.

The mechanism for the pinacol-pinacolone rearrangement which finds most favor today is a synthesis of the ideas of several workers in this field over a period of fifty years (*1, 8, 9, 10, 12, 13, 17, 18, 19, 20, 22, 24*). The essential steps are

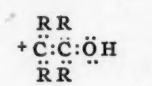


(I)

(II)

(III)

Step II is the *simultaneous* loss of a water molecule from carbon 1 and migration of an aryl group with its electrons from carbon 2 to carbon 1 to prevent the building up of a high positive charge on carbon 1. The work of Nametkin and Delektorsky, Bartlett and Poeckel and Bartlett and Bavley (*8*) with the cyclic pinacols such as *cis*- and *trans*-1,2-dimethyl-1,2-cyclohexandiols in which only the alkyl group trans to the hydroxyl group is shown to migrate, and that of Bernstein and Whitmore (*10*) in which it is shown that a Walden inversion occurs in the rearrangement of 1,1-diphenyl-2-amino-1-propanol induced by treatment with nitrous acid, clearly demonstrate that inversion at carbon 1 occurs during pinacol-pinacolone rearrangements.* These observations lend support to the view that the loss of the water molecule and the migration of the hydrocarbon radical occur simultaneously, for the existence of the ion



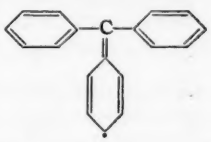
for any appreciable length of time would surely lead to racemization. It follows that the rearrangement takes place intramolecularly, and a reasonable picture would visualize the water molecule moving away from carbon 1 of ion B at the time that negative charge is drawn *intramolecularly* from carbon 2 toward carbon 1 to prevent the accumulation of positive charge on carbon 1.

* It had been previously shown by McKenzie, Roger, and Wills (*20*) that no racemization occurs when 1,1-diphenyl-2-amino-1-propanol rearranges.

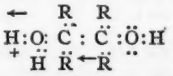
A radical must migrate at the same time, moving along with the negative charge from carbon 2 to carbon 1, for there would not be enough negative charge left on carbon 2 to retain it. The migrating group attaches itself to carbon 1 as far as possible from the position being vacated by the water molecule, thus accounting for the inversion at carbon 1. The concept of the intramolecular withdrawal of negative charge from carbon 2 toward carbon 1 is of importance to the present discussion.

In 1928 Ingold (*18*) observed that it should be possible to predict the probable course of the rearrangement of an unsymmetrical pinacol, RRC(OH)C(OH)R′R′, by utilizing the principle that the radicals displaying the greatest electron release should facilitate the removal of the hydroxyl from the carbon to which those radicals are attached. For example, if R displays greater electron release than R′, the final product should contain a greater proportion of RRR′CCOR′ than R′R′RCCOR. This principle has proved to be valid for most unsymmetrical benzopinacols. It is apparent that this method of approach cannot be used for symmetrical pinacols RR′C(OH)C(OH)RR′, for in such molecules the effects of electron release upon the two hydroxyl groups must be identical.

A theoretical approach to the problem of the determining factors in rearrangements of symmetrical pinacols has been made by Hatt, Pilgrim, and Stephenson (*17*) who have pointed out that the order of effectiveness with which aryl groups stabilize triarylmethyls roughly parallels the migration aptitudes of the same groups. The reason for this parallel behavior appears to be associated with the ability of the radical in question to serve as a source of negative charge which would (*a*) stabilize the triarylmethyl radical through the formation of resonance isomers, such as

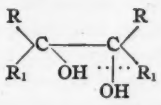


and (*b*) neutralize the incipient positive charge on the pinacol carbon which first loses a water molecule:



However, this relationship should exist only in the absence of marked steric effects, for a radical which, by its bulk, might bring about some stabilization of the triarylmethyl radical might also, because of its bulk, be unable to migrate easily. In fact, Hatt, *et al.*, have found that the order *p*-biphenylyl > *m*-biphenylyl > phenyl for free radical stabilization becomes *p*-biphenylyl > phenyl > *m*-biphenylyl for migration aptitudes, an observation which they explain as being due to steric hindrance of the *m*-biphenylyl radical. They have further found that no migration whatsoever of the *o*-biphenylyl group is observed when symmetrical di-*o*-phenylbenzopinacol is rearranged, the phenyl group migrating exclusively. They believe the inability of the *o*-biphenylyl group to migrate is likewise due to steric hindrance.

A general application of the principle of electron release to explain the rearrangements of isomeric symmetrical and unsymmetrical pinacols has been suggested by Stearns, Ri, and Eyring (*13*). For the unsymmetrical pinacol, RRC(OH)C(OH)R_1R_1, they use Ingold's treatment (*18*) as previously described, the group R with the smallest electron release being the predominant migrating group; however, they assume a different mechanism from that presented here. Their complete discussion of the rearrangement of the isomeric symmetrical pinacol follows verbatim: "For the symmetrical pinacols,



each C—OH bond has an equal chance of breaking, and the end result will be the same whichever bond breaks. When the OH splits as an ion at the point indicated by the dotted line, taking with it a proton from the other OH to form water, this will leave a negative charge accumulated on the carbon atom which retains its oxygen, so that now R, being less electrophilic than R_1, will migrate predominantly. Thus, it will happen frequently that in a symmetrical pinacol one group migrates predominantly whereas in the unsymmetrical isomer another group undergoes change." Their conclusion is qualitatively satisfactory, but their mechanism appears to offer no explanation of the manner in which an acid catalyst plays such an important part in the reaction. In fact, it seems more probable that the determining factor in the reaction is not a large negative charge on the carbon retaining an oxygen, but rather an incipient large positive charge on the carbon which loses its hydroxyl. Let us, therefore, consider the problem in terms of the mechanism outlined previously.

Suppose that in the two isomeric pinacols, $RRC^1(OH)C^2(OH)R'R'$ (*A*) and $RR'C^1(OH)C^2(OH)R'R$ (*B*), R effects greater electron relase than R′. As Ingold (*18*) has pointed out, the groups R in pinacol *A* would accordingly supply more negative charge to carbon 1 than the R′ groups would supply to carbon 2. This in turn would increase the negative charge density at carbon 1 and weaken the C—O bond, thereby making it easier for the hydroxyl ion to be eliminated from this carbon. This scission would necessitate the migration of R′, and one might therefore expect more of the ketone RRR′CCOR′ than RR′R′CCOR.

There is, however, no possible electrical effect which might determine which hydroxyl of pinacol *B* would most likely be removed, for both carbons 1 and 2 possess identical electron densities. The controlling factor here should then be the relative ease with which R or R′ on carbon 2 can supply negative charge intramolecularly to carbon 1, from which the hydroxyl is being removed, in order to prevent the accumulation of positive charge

TABLE 1

COMPARISON OF MIGRATION APTITUDES DETERMINED FROM SYMMETRICAL PINACOLS AND BIPHENYLENE PINACOLS (*6*)

	Migration Aptitude in		
Symmetrical pinacol		Biphenylene pinacol	
$RR'C(OH)C(OH)R'R$			
Group	(M_s)	M_b	$1/M_b$
Phenyl	1.0	1.0	1.0
m-Tolyl	1.95	0.33	3.0
p-Tolyl	15.0	0.046	22
p-Phenetyl	66	0.012	83
p-Anisyl	70+	0.006	170

on carbon 1. Consequently, since R effects greater electron release, R should be best able to supply this necessary negative charge, and since, as explained earlier, the process is completely intramolecular, R should likewise be the predominant migrating group rather than R′ as in the case of the symmetrical pinacol. The final product should then show a preponderance of RRR′-CCOR′. Thus the migratory aptitude of R′ should be larger if results from the rearrangement of the unsymmetrical rather than the symmetrical pinacol were used as the criterion, whereas that of R would have a larger value if the comparison were made by use of the symmetrical pinacol. This inversion is illustrated in Table 1 in which are shown some migration aptitudes calculated by Bachmann and Sternberger (*6*) using the experimental data from the rearrangements of biphenylene pinacols for one set and those from symmetrical pinacols for the other set.

These conclusions drawn from a consideration of electrical effects would, of course, be completely valid only when no other factors influence the relative rates of migration of the two radicals in question. It is probable that in most pinacols other conditions also contribute to the course of the reaction, but it should nevertheless follow that the radical R effecting the greater electron release should have a greater migration aptitude in the symmetrical than it does in the unsymmetrical pinacol. The reverse should then be true of the radical R′ having the smaller electron release. As a result, it is entirely within expectancy that R may migrate to a greater extent than R′ in both of the isomeric pinacols, but with the proportion of R migration less in the unsymmetrical than in the symmetrical pinacol.

In order to obtain a measure of the relative electron releases of several aryl groups, one can make use of the dissociation constants of the carboxylic acids corresponding to the groups in question. Since the acidities of substituted benzoic acids decrease with increased electron release to the carboxyl carbon (*16*), it follows that of two acids, RCOOH and R′COOH, the one having the lower dissociation constant likewise contains the radical displaying greater electron release. If R is the radical having the greater electron release and the two previous isomeric pinacols *A* and *B* (page 435) are caused to rearrange, then the amount of R migration should be more during the rearrangement of *B* rather than *A*, while R′ should migrate to a larger extent when *A* rather than *B* rearranges.

TABLE 2

REARRANGEMENTS OF SOME ISOMERIC SYMMETRICAL AND UNSYMMETRICAL PINACOLS COMPARED TO THE DISSOCIATION CONSTANTS OF THE BENZOIC ACIDS CONTAINING THE SAME RADICALS

Groups	Per cent rearranged in unsymmetrical pinacol, RRCOH-COHR′R′	Reference	Per cent rearranged in symmetrical pinacol, RR′COH-COHRR′	Reference	$K \times 10^5$ for acids RCOOH and R′COOH
p-Anisyl	45		96.7		3.38
p-Tolyl	55	(*5*)	3.3	(*4*)	4.24
Phenyl	51		6		6.27
p-Tolyl	49	(*2*)	94	(*4*)	4.24
Phenyl	72		1.4		6.27
p-Anisyl	28	(*2*)	98.6	(*4*)	3.38
Phenyl	50		34		6.27
m-Tolyl	50	(*2*)	66	(*4*)	5.35
Phenyl	91		35		6.27
p-Fluorophenyl	9	(*5*)	65	(*5*)	7.22
p-Biphenylyl	58		87		...
m-Tolyl	42	(*5*)	13	(*4*)	5.35
Phenyl	57		60		6.27
p-Chlorophenyl	43	(*5*)	40	(*21*)	10.5
Phenyl	46		8		6.27
p-Biphenylyl	54	(*5*)	92	(*14*)	...
p-Anisyl	35		99		3.38
m-Tolyl	65	(*5*)	1	(*3*)	5.35
p-Ethoxyphenyl	33		98.3		...
Phenyl	67	(*5*)	1.7	(*3*)	6.27

TABLE 3

REARRANGEMENTS OF SYMMETRICAL PINACOLS COMPARED TO THE DISSOCIATION CONSTANTS OF THE BENZOIC ACIDS CONTAINING THE SAME RADICALS

Groups	Per cent rearranged in symmetrical pinacol	Reference	$K \times 10^5$
p-Anisyl	67		3.38
α-Naphthyl	33	(*7*)	20
m-Methoxyphenyl	38 (83)		8.17
Phenyl	62 (17)	(*3, 7*)	6.27
p-Tolyl	75		4.24
p-Ethylphenyl	17	(*7*)	4.43
p-Ethylphenyl	83		4.43
Phenyl	17	(*7*)	6.27
p-Isopropylphenyl	90		4.43
Phenyl	10	(*7*)	6.27
α-Naphthyl	53		20
p-Tolyl	47	(*7*)	4.24
m-Methoxyphenyl	39		8.17
m-Tolyl	61	(*3*)	5.35
p-Anisyl	99		3.38
m-Tolyl	1	(*3*)	5.35
p-Chlorophenyl	1		10.5
Anisyl	99	(*3*)	3.38
p-Chlorophenyl	1.7		10.5
p-Tolyl	98.3	(*3*)	4.24
m-Methoxyphenyl	10		8.17
p-Tolyl	90	(*3*)	4.24
α-Naphthyl	33		20
p-Anisyl	67	(*7*)	3.38
p-Bromophenyl	41		10.7
Phenyl	59	(*15, 21*)	6.27
p-Bromophenyl	4.5		
p-Biphenylyl	96.5	(*15*)	
m-Bromophenyl	0		
p-Biphenylyl	100	(*15*)	
p-Tolyl	57		
p-Biphenylyl	43	(*4*)	
p-Anisyl	96.8		
p-Biphenylyl	3.2	(*4*)	
m-Methoxyphenyl	13.5		
p-Biphenylyl	86.5	(*3*)	
p-Ethoxyphenyl	97		
p-Tolyl	3	(*3*)	
m-Chlorophenyl	0		
p-Biphenylyl	100	(*3*)	

In Table 2 are collected the available data concerning the rearrangements of isomeric pairs of symmetrical and unsymmetrical substituted benzopinacols along with values for the dissociation constants of the corresponding acids as given by Dippy (*11*). In all but one of these pairs for which the data are complete, the group which migrates to a greater extent during the rearrangement of the unsymmetrical rather than the symmetrical pinacol is the one present in the acid having the higher dissociation constant. And of course the other group, which shows a greater tendency to migrate during the rearrangement of the symmetrical rather than the unsymmetrical pinacol, is found in the acid having the lower dissociation constant. The behavior of the *p*-fluorophenyl radical is anomalous, for in the comparison of the migrations of this radical in the symmetrical and unsymmetrical pinacols, the expected inversion of amount of migration exists, but the usual correlation between dissociation constant and migration tendency is lacking. The data for other symmetrical pinacols are shown in Table 3. In all but one example the radical which migrates to the larger extent is the one having the greater electron release, as shown by the lower value of the dissociation constant of the benzoic acid which contains the radical in question.

It can be seen from Table 2 that the values of migration aptitudes are in general more divergent when measured using symmetrical rather than unsymmetrical pinacols. A further difference between symmetrical and unsymmetrical pinacols has been pointed out by Bachmann, Ferguson (*3*), and Moser (*4*). They have shown that migration aptitudes for two radicals R′ and R″ measured by examining the rearrangements of the symmetrical pinacols $(R'\text{Ø}\overset{|}{\text{C}}\text{OH})_2$ and $(R''\text{Ø}\overset{|}{\text{C}}\text{OH})_2$ can be used to predict quite accurately the products which will result from the rearrangement of $(R'R''\overset{|}{\text{C}}\text{OH})_2$; however, such calculations made from similar data obtained from unsymmetrical pinacols do not agree at all closely with experimentally measured values, although they do qualitatively indicate the general course of the rearrangement. Some examples of the comparison of the results of such calculations with experimental data for both symmetrical and unsymmetrical pinacols are shown in Table 4.

It appears from these data that the radicals have less effect in determining the course of rearrangement of unsymmetrical than of symmetrical pinacols. The electronic mechanism offers the following possible explanation. The only way a given group can influence the rearrangement of unsymmetrical pinacols is by facilitating the removal of a particular hydroxyl; however, the real activating factor for the splitting off of the hydroxyl is most likely the weakening of the C—O bond brought about by attachment of some acid, such as a proton, to the hydroxyl, forming an oxonium ion such as that shown as the product of step I of the mechanism on page 434. There is no reason to believe that the electrical nature of the attached groups will materially prevent attack of any hydroxyl by the acid. It follows that if oxonium ion formation is the most important activating factor, the electrical influence of the attached groups upon the course of the reaction may conceivably be reduced or, in some cases, even nullified. The obvious result would be a closer approach to random hydroxyl removal, resulting in a smaller difference in the amounts of the two possible products formed. On the other hand, the relatively large number of clear-cut differences in the tendencies of groups to migrate during rearrangements of symmetrical pinacols, as seen in Table 3, can also be explained in a qualitative way by the electronic mechanism. The removal of the hydroxyl from such pinacols must be a completely random process; consequently, the course of the rearrangement should be more dependent upon the electron releases of the attached groups which are in position to migrate. The result might well be the much more decisive correlation of electron release with migration aptitude as shown by the experimental data.

TABLE 4

MIGRATION OF GROUPS

Migrating groups	*Comparison group*	*Per cent predicted*	*Per cent found*
For Groups in Symmetrical Pinacols (*4*)			
p-Tolyl		58	57
p-Biphenylyl	Phenyl	42	43
m-Tolyl		37	34
Phenyl	*p*-Biphenylyl	63	66
Anisyl		97.5	96.8
p-Biphenylyl	*p*-Tolyl	2.5	3.2
p-Bromophenyl		6	4.5
p-Biphenylyl	Phenyl	94	95.5
p-Ethylphenyl		24	25
p-Tolyl	Phenyl	76	75
Anisyl		96.3	67
α-Naphthyl	*p*-Tolyl	3.7	33
For Groups in Unsymmetrical Pinacols (*5*)			
p-Biphenylyl		54	58
m-Tolyl	Phenyl	46	42
Anisyl		29	45
p-Tolyl	Phenyl	71	55
Anisyl		28	35
m-Tolyl	Phenyl	72	65

In conclusion, it should be emphasized that the experimental results available are still quite meager and need to be supplemented in order that the theory may be given a fair test. There are, for example, no data upon which to base any conclusion concerning which step in the mechanism is rate-controlling, and it would therefore appear that some kinetic studies might be of value. It would also be useful to have data concerning the rearrangements of benzopinacols containing a wider variety of substituents than are now available. Nevertheless, the theory so far appears to be qualitatively in agreement with the existing experimental data.

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If I Had a Son

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IF I had a son—or a daughter, or a protégé—I could not educate him in the public schools.

No matter what path in life a man may take, no matter what calling he follows, he must make use of symbols. The more technical and specialized his calling, the more elaborate will be the system of symbols he is obliged to use and the more important it will be that his preliminary training in the use of symbols be thorough. Even in the sciences, facts are not enough. It is extremely doubtful, for instance, if chemistry could have developed to its present state using the language of Hermes Trismegistus. There is nothing more instructive in this respect than to study the history of chemical nomenclature. This is true of other sciences; biology made little headway until Linnaeus published his *Systema Naturae*.

But one does not learn a complex, technical language until he can understand the common language upon which it is built. No one expects to teach the calculus to a child who has not mastered the multiplication table, nor does he advise the semiliterate to read Milton. It is the avowed purpose of the public schools to teach this fundamental, common language; and they have failed to do so.

What other conclusion can one make when time after time he encounters students who do not know the difference (in use) between a phrase and a clause, who think that the words "beneficial" and "important" are synonyms, and who stumble when asked to read aloud the simplest paragraph? Such have been my experiences time and time again. I have heard seniors at a state college read a simple "Life of Jesus" in a manner which would scarcely do credit to a child in the second year of grammar school. One class in secondary school biology interpreted the statement of the textbook that certain aquatic insects "seek the protection of vegetation" as meaning that said creatures are herbivorous!

Greek and Latin are no longer studied. The lack could be made up, however, if children were taught to use the root words which appear even in newspapers. Surely it is not too much to expect them to know the difference between such prefixes as *inter* and *intra*, and such words as *affect* and *effect*. But they do not!

Both in and out of school I was saturated with Greek and Roman mythology. If one were, tomorrow, to ask the average college class why the element mercury is so named, he would be met by blank expressions of face. Such knowledge is not mere decoration. Literature is so saturated with reference to Hellenistic culture that at least a bowing acquaintance with classical mythology is an excellent system of mnemonics.

It seems obvious that a good scientist should know something of the history of science and also of the social and political history which accompanied it. Yet few of our children are, today, learning even the essentials of American history. Of other branches of the subject they know nothing.

Common arithmetic is not learned, as one who teaches higher mathematics knows only too well. With a reasonable knowledge of numbers for his age, a ten-year-old boy of average intelligence can be taught to solve simple, chemical equations. Yet year after year college teachers spend time which should be devoted to other matters drilling boys and girls in what amounts to simple arithmetic and algebra.

We have been considering the problem of training from the standpoint of chemistry, but the foregoing considerations apply to practically any field one wishes to name. A ceramic engineer, an entomologist, an army officer, a dramatist, a clergyman—each and every one needs for a foundation a common denominator of language thoroughly learned. But "educators" evidently do not believe this. Neither, unfortunately, do some parents and taxpayers. They think it sufficient for children to learn to build chicken coops.

If I had a son, I should have to supplement his public schooling with materials added at my own time and expense. Otherwise he might never become educated—even to the extent of mastering the techniques of making a living. And if he succeeded without my aid, it would not be because of the public schools, but in spite of them.

Organization of the Technical Report

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THIS paper suggests an outline to be followed in writing a technical report. It concerns principally the report of an experiment and may have little bearing on other types of technical writing, such as presentations of theories, descriptions of apparatus, book reviews, abstracts, topic reviews, textbooks, and records of patents.

The ideal technical report should be accurate, short, concise, straightforward, scientifically sound, and should contain certain essential sections placed in a logical order. The reader should obtain at *first* reading a clear picture of the purpose, the general method of attack, and the over-all conclusions. The organization should be such that he can then readily refer to any section for specific details.

There is a great diversity of methods of building a technical report and there is a great diversity of purposes in publishing these reports, but unfortunately the method seldom fits the purpose. Perhaps the worst mistake is lack of logical organization; the result of this mistake is that the reader becomes confused and loses the whole perspective of the paper. There is often a haphazard jumble of conclusions, problems, data, purposes, procedures, and discussions. Another serious error is excessive length. Many papers are so filled with undesirable detail and repetitions caused by lack of organization that potential readers, after a glance at the clock, decide not to tackle them. Some papers omit essential sections, such as a statement of the problem. Data are often presented sloppily by poor graphs, or by a strange, unrelated mixtures of tables, figures, and general word descriptions.

Technical report writing can be improved by various means. It is essential that the potential writer know how to think and plan logically. He should be adequately trained in grammar and composition. Then he should study the technique of writing technical reports and, after this, practice writing extensively. He should carefully analyze the nature of his reader and, if the report is to appear in print, the policy and purposes of the journal in which it will be published. He should list the essential ideas, arrange them in a logical order, then write the text in detail. It is excellent practice to have both the outline and the final report checked by persons acquainted with the subject.

I. Summary
II. Introduction
  A. Statement of problem
  B. Analysis of problem
  C. Review of previous work
  D. Approach used in this work
III. Experimental work
  A. Apparatus and equipment
  B. Materials and reagents
  C. Procedure
  D. Data
IV. Discussion
  A. Theoretical background
  B. Obscure and involved parts of experimental work
  C. Meaning of data
  D. Errors (known and possible)
  E. Deficiencies of the work
  F. Suggested further study
V. Conclusions
VI. References

Above is given an outline which can be used as a guide for most reports of experiments. It contains all the essential sections, arranged in such a manner that the reader can follow the sequence of ideas readily. For some purposes, part of the sections may be short or omitted entirely, and rearrangement may be desirable. It is emphasized that a writer should not draft his reports by following this outline step by step, as though writing according to a mathematical formula, for dry uninteresting papers may result if all personal initiative of the writer is denied. This outline is meant to be a guide, not a formula.

The *summary* usually serves one of two purposes: readers who are interested generally, but not specifically may read only this section; and it serves to fix the sequence of the paper in the mind of the reader of the complete paper. It should state the problem, give the essence of the experimental work, and generalize the important conclusions.

In the introduction, the *statement of problem* must be specific. The haziness, or even the complete lack, of this statement is probably the most common and most serious error in technical writing. It serves to emphasize the purpose of the paper to the reader and to prepare him for what is to follow.

The *analysis of problem* explains why the problem exists and tells what advantages its solution will present. This analysis is flexible and may contain much necessary descriptive and background material.

The *review of previous work* may be omitted in many articles; in some it has no place at all. It is, however, generally desirable to refer to basic references on the subject in question. It is often good practice to list a fairly comprehensive bibliography and occasionally to report an exhaustive literature search. The decision of what to include is best made by studying carefully the purpose of publishing the paper.

The *approach used in this work* may be omitted in very short papers, but usually a brief statement describing the perspective of the *experimental work* section makes the latter much easier to understand.

The section labeled *experimental work* is the one best

written in most articles. It should be written so that a worker skilled in the art can repeat the work and obtain the same results by following the *procedure* given by the author. *Apparatus and equipment* can often be described to advantage by photographs and drawings. The general nature, the methods of preparation, and the purity of *materials and reagents* should be described carefully. Many *procedures* are discussed in such unnecessary detail that much space is wasted, although some omit essential steps.

The presentation of *data* involves many difficult problems. Results should be given correctly, understandably, and in sufficient detail to justify the conclusions. Data may be inserted in the *procedure* immediately following the description of the experimental work used to obtain them or grouped at the end of the *procedure;* the better position will depend on the nature and purpose of the paper. The form of the *data*—tables, figures, graphs, and photographs—should be carefully considered. In most cases graphs serve best to emphasize comparisons and to conserve space. Long, involved tables tend to confuse the reader. Photographs are almost invariably better than word descriptions. General graphing practice is so poor that data are seldom presented to advantage. The title of the figure should describe its contents; the axes should be labeled completely, with units given; grid lines should be used, but not so thickly as to cause confusion; points should be used on the curves unless the data are continuous; the curves should be heavier than the grid lines; and the abscissa should be used for the independent variable.

The *discussion* is the most difficult part of a paper to write. Careful judgment must be exercised in its length, for a discussion can easily become excessively long. The *theoretical background* can usually be short, and mathematics can be used to advantage if applicable. References are often essential at this point.

Obscure and involved parts of the procedure are best discussed in this section, this being preferable to breaking the continuity of the *procedure* itself. Many papers will not require this part of the discussion at all.

The *meaning of the data* is a most important topic. It serves to bridge the gap between the conclusions and the naked data. It explains exactly how the data fit the problem.

The *errors* always present in experimental work are completely ignored by many—even most—authors. A large percentage of papers are nearly worthless because there is no indication of the accuracy and precision of the data, and repetition of the work is thus necessitated. Not only the known errors or limits of accuracy, but also possible errors, should always be discussed, or at least mentioned. Any scientist who flagrantly omits all mention of his errors is leaving himself wide open to adverse criticism.

Deficiencies of the work—deficiencies apart from errors in the data—should be discussed next. These should include deficiencies of perspective, of attack, and of completeness. If a writer does not acknowledge these things, others will point them out for him—to his embarrassment.

Lines of future study on the problem in question may or may not be pointed out, but if these plans for future work are derived directly from the study, such suggestions or proposals are in order and may be helpful to other workers.

The *conclusions* are the most important part of the paper. Extreme care must be used, for by drawing the wrong conclusions the writer can get himself into hot water, hot and deep. By publishing one paper with incorrect conclusions, the budding scientist can easily kill his chances for establishing a reputation. A recognized authority can usually weather the storm caused by one or two bad papers, but even he can fall ignominiously. First, the conclusions should answer the problem as stated in the *introduction*. Second, they should be completely validated by the data given, perhaps supplemented by references to other work. Third, they should be stated in such a manner that they can be individually isolated from the body of the paper and still be valid, for that is just what may happen to them in reviews, abstracts, and discussions.

References may be inserted in the text, given as footnotes, or listed at the end of the paper. The last method is usually used and is usually preferable, for in this manner it serves best as a guide to workers interested in using it to make a comprehensive study of the subject. The references may be listed chronologically by subject, or alphabetically by author. The last method is generally accepted, but others may serve best for special cases. A standard method of giving references (see *Chemical Abstracts* for chemical writing) should be strictly followed to avoid confusion and errors in "interpretation."

The first and foremost requirement of all technical reports is accuracy. Proofreading by several persons is helpful in reducing the number of errors in numerals, spelling, and grammar. The author must carefully guard against weakness in organization, coherence, and perspective. The report must be understandable—must convey the author's ideas to the reader. Careful organization and careful writing will take care of this. Because of the immense volume of technical literature, it is desirable that reports be as brief as possible. This requirement may sometimes demand extreme brevity, or even omission, of some of the sections in the outline suggested above; but continuity is important, and adequate statements of problem, data, and conclusions must never be sacrified. By proper training of writers, by use of logic and organization, and by care in writing, technical reports can be transformed from a jungle of facts, figures, and fumblings to papers that reflect the scientific method used by their authors.

INORGANIC NITROSYL COMPOUNDS

I—Cationic and Anionic Compounds

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INTRODUCTION

SUBSTANCES containing the NO group are usually referred to as nitrosyl compounds when the addendum is inorganic in nature and as nitroso compounds when the addendum is organic in nature. The inorganic nitrosyl derivatives are of particular interest because examples are known in which the nitrosyl grouping behaves as a positive material, as a negative material, and as an apparently neutral material (*7, 10, 30, 33, 38, 41, 43, 47, 48, 54*). The existence of such a variety of compound types indicates that the nitrosyl group is almost unique in character and prompts a summary of the properties and structures of these materials.

Inasmuch as many of them are produced by direct reactions involving nitric oxide, the inorganic nitrosyl compounds can perhaps best be approached through a preliminary consideration of some of the characteristics of this gas. Although nitric oxide contains an odd number of electrons, its lack of color, its slight tendency (at room temperature at least) to dimerize, and its lack of reactivity with many materials suggest inherent differences between it and other odd molecules. Electronically, one might represent nitric oxide as either

$$:\dot{N}::\ddot{O}: \quad \text{or} \quad :\ddot{N}::\overset{+}{O}:$$
$$\text{I} \qquad\qquad \text{II}$$

with structure I being the more probable in view of the unfavorable charge distribution in structure II (*31*). Pauling (*31*) points out, however, that small stability differences permit resonance between these two structures, imparting the effective structure

$$:\dot{\dot{N}}::O: \quad \text{or} \quad :N\equiv\equiv O:$$
$$\text{III}$$

to the material. The general characteristics of nitric oxide, including the observed internuclear distance of 1.14 A. (between the double and triple bond distances of 1.18 A. and 1.06 A., respectively) are in accord with this structure (*31*).

On the basis of this information, one can conclude that nitric oxide might enter into chemical combination in any one of the following fashions:

1. As a positive ion, NO^+, through loss of the unpaired electron. Inasmuch as the internuclear distance in the excited nitric oxide molecule equals the triple bond distance (*31*), it seems reasonable to formulate the nitrosyl cation as

$$(:N:::O:)^+ \quad \text{or} \quad (:N\equiv O:)^+$$
$$\text{IV}$$

In actual compounds, actual or effective electron loss, producing ion or highly polar linkages, respectively, might be expected, depending upon the nature of the electronegative material present.

2. As a negative ion, NO^-, through gain of an electron from some electropositive material. Although exact structural information is lacking, such an anion might be formulated as

$$(:\dot{\dot{N}}::\dot{\dot{O}}:)^- \quad \text{or} \quad (:\dot{\dot{N}}=\dot{\dot{O}}:)^-$$
$$\text{V}$$

3. As a coordinating group, through the donation of an electron pair. Such a condition might arise from direct donor behavior by the nitric oxide molecule or from coordination of either the NO^+ or the NO^- radical (*34, 38, 41*).

The inorganic nitrosyl compounds can be conveniently classified and discussed in terms of these considerations. In this paper cationic and anionic derivatives will be described. In a subsequent communication, materials containing coordinated NO groups will be considered.

SIMPLE COMPOUNDS CONTAINING THE NO^+ GROUP

In a number of compounds, existence of the NO^+ group has been fairly well established (*24*). Among other similar but less extensively investigated substances, its existence may be inferred by analogy. Examples of both classes may be cited.

A. The Existence of the NO^+ Group Appears Well Established: One of the best known examples of such materials is the so-called nitrosyl sulfuric acid, nitrosyl bisulfate, or nitrose, the formula for which may be written $NOHSO_4$. This compound can be obtained by a variety of procedures, among them reaction between fuming nitric acid and sulfur dioxide, reaction between either nitrogen trioxide or nitrogen tetroxide and concentrated sulfuric acid, and reaction between nitrosyl chloride and concentrated sulfuric acid (*9, 19, 54*). When pure, it is a white crystalline solid melting with decomposition at 73°C. Its formation and hydrolysis are characteristic of the chamber process for the production of sulfuric acid (*54*). It is soluble without decomposition in concentrated sulfuric acid.

Much of the literature relative to the structure of nitrosyl sulfuric acid is highly controversial. For a time the substance was regarded as an equilibrium mixture of nitro and nitroso forms

$$HOSO_2NO_2 \rightleftharpoons HOSO_2ONO$$

largely because of the observed formation of both *p*-

nitro and *p*-nitroso derivatives when treated with dimethyl aniline (*6*). That the nitro derivative is not a primary product in the reaction (*9*) coupled with the production of nitrosyl bromide or chloride upon treatment of the acid with the corresponding sodium halide and the formation of the acid by reaction between silver bisulfate and nitrosyl chloride (*9*) lends convincing support to the nitrosyl (nitroso) formulation.

That nitrosyl sulfuric acid possesses ionic characteristics is shown by abnormalities in its molecular weight in concentrated sulfuric acid, which indicate dissociation as a binary electrolyte (*16*). These results have been interpreted as indicating the structure $NO^+HSO_4^-$ (*17*). Further evidence is given by Raman data (*1, 2*), the strong line at 2340 cm.$^{-1}$ being regarded as characteristic of the NO^+ grouping.

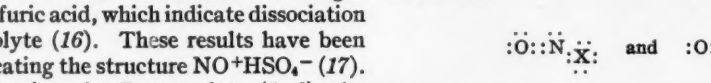
Perhaps even better known are the nitrosyl halides—NOF, NOCl, and NOBr (*13, 14, 15, 33, 54*). Nitrosyl fluoride can be obtained by direct combination of nitric oxide with fluorine (*37*), by reaction of nitrosyl chloride with silver fluoride (*33, 54*), by reaction of nitrosyl fluoborate with sodium fluoride (*5*), or by reaction between potassium fluoride and the compound $NOSbF_6$ (*36*). Nitrosyl chloride can best be prepared by direct combination of nitric oxide with chlorine (*54*), by reaction of nitrosyl sulfuric acid with either sodium or hydrogen chloride (*8*), or by reaction of nitrogen dioxide with moist potassium chloride (*50, 51*), although many other preparative procedures are available (*14, 33, 54*). Nitrosyl bromide can be obtained by direct reaction between nitric oxide and bromine, although reversibility of the reaction reduces the purity of the product (*54*). The iodide has never been prepared. Characteristic physical constants for the nitrosyl halides are summarized in Table 1 (*13, 14, 15, 20, 21, 22*).

TABLE 1

PHYSICAL PROPERTIES OF THE NITROSYL HALIDES

Property	*NOF*	*NOCl*	*NOBr*
Molecular weight	49.008	65.465	109.924
Melting point (°C.)	−132.5	−64.5	− 55.5
Boiling point (°C.)	− 59.9	− 6.4	ca. 0
Color in gas phase	Colorless	Orange-yellow	Red
Bond distances (A.)			
X—O	....	2.65 ± 0.01	2.85 ± 0.02
X—N	....	1.95 ± 0.01	2.14 ± 0.02
N—O	....	1.14 ± 0.02	1.15 ± 0.04
Bond angle (°)	....	116 ± 2	117 ± 3
Dipole moment (*D*)	....	1.83	1.87

Although the physical constants of the nitrosyl halides are those of covalent compounds, they are also those of polar materials. Perhaps the best structural information is given by the bond distances and dipole moments listed for nitrosyl chloride and bromide (*20, 21, 22*). The measured N—Cl and N—Br bond distances of 1.95 A. and 2.14 A., respectively, as determined from electron diffraction data, are somewhat larger than the sums of the covalent single bond radii of 1.69 A. (for N—Cl) and 1.84 A. (for N—Br) (*20, 21, 22*). Since an ionic bond between nitrogen and chlorine would amount to 2.64 A. (based upon a radius of 1.40 A. for the NO^+ ion) (*22*), it is apparent that the actual nitrogen to chlorine bond lies between a purely covalent bond and a purely ionic bond. The same is true for the nitrogen to bromine bond in nitrosyl bromide. Furthermore, the nitrogen to oxygen bonds in both compounds have lengths between the double and triple bond values already quoted, indicating some triple bond character. These facts can be accounted for (*21, 22*) by an assumed resonance between the structures



X denoting either Cl or Br. About 50 per cent ionic character in both nitrosyl chloride and bromide is indicated by agreement between a calculated nitogen to oxygen distance of 1.11 A. and the measured values (*22*).

These views are supported by the high values observed for the dipole moments of the two compounds (*21*). Since the calculated dipole moments for purely covalent nitrosyl chloride and nitrosyl bromide are 0.3 *D* and 0.4 *D*, respectively (*21*), highly polar or partially ionic character is indicated in both instances. Corresponding data for nitrosyl fluoride are not available, but the physical constants given for this compound (Table 1) indicate less partial ionic character than shown by the other nitrosyl halides.

Further evidences of partial ionic character are given by the reaction of nitrosyl bromide with bromine to give nitrosyl tribromide, $NOBr_3$ (*44*), and by the existence of a number of double chlorides with nitrosyl chloride (*4, 12, 14, 35*). While the chlorides of zinc, aluminum, and divalent mercury form loose addition compounds with nitrosyl chloride, and cuprous and manganous chlorides yield products containing coordinated nitrosyl groups (*4*), magnetic evidences (*4*) indicate that certain other chlorides form nitrosyl salts, such as $NO^+[SbCl_6]^-$, $(NO)_2^+[SnCl_6]^-$, and $(NO)_2^+[PtCl_6]^-$. On the other hand there is some evidence that the compound $NOSbCl_6$ resonates between a salt and a molecular addition compound (*40*).

Another interesting compound is nitrosyl perchlorate, $NOClO_4$. This is a white, hygroscopic crystalline compound which is formed by reaction of nitrogen dioxide with concentrated perchloric acid (*3, 17, 18*) or by reaction of nitrosyl chloride with silver perchlorate (*32*). Evidences for ionic character in nitrosyl perchlorate are many. Thus, it gives conducting solutions when dissolved in nitromethane (*17*); it has the same crystalline structure as both hydronium perchlorate, H_3OClO_4, and ammonium perchlorate, NH_4ClO_4, the nitrosyl grouping being ionic with the same size as the H_3O^+ ion but larger than the NH_4^+ ion (*23*); and it gives a Raman spectrum comparable with that given by nitrosyl sulfuric acid and indicative of the presence of the NO^+ group (*3*).

Similar in its characteristics is nitrosyl fluoborate, $NOBF_4$ (*46*). This is a hygroscopic crystalline moc-

pound which can be prepared by reaction between fluoboric acid and either nitrogen trioxide (*5*, *52*) or dioxide (*45*) or by reaction between ethyl nitrite and acetyl fluoborate (*39*). Nitrosyl fluoborate has the same crystalline structure as the ionic hydronium and ammonium fluoborates and may, therefore, be considered to be ionic itself (*23*).

B. The Existence of the NO^+ Group Lacks Definite Confirmation: A number of nitrosyl compounds, which by their modes of preparation and general characteristics may be regarded as analogs of those compounds already described, are discussed in the literature. For these materials, structural data are lacking, but it seems not unreasonable to ascribe cationic or partially cationic characteristics tentatively to the nitrosyl groupings in them. Among these substances are:

1. Dinitrosyl selenate, $(NO)_2SeO_4$, which is described as a blue, easily hydrolyzed solid obtained by the reaction of liquid nitrogen tetroxide upon 83 per cent selenic acid at the temperature of solid carbon dioxide (*27*). The melting point is given as −13°C.

2. Nitrosyl selenic acid, $NOHSeO_4$, which has been obtained by adding a large excess of liquid nitrogen trioxide to 100 per cent selenic acid and allowing the excess to evaporate (*29*). It is described as a white crystalline compound, melting with decomposition at 80°C., dissolving in concentrated sulfuric or selenic acid, and decomposing in contact with water. This compound is a formal analog of nitrosyl sulfuric acid.

3. Nitrosyl sulfuric anhydride or nitrosyl pyrosulfate, $(NOSO_3)_2O$ or $(NO)_2S_2O_7$, which has been obtained by thermal decomposition of nitrosyl sulfuric acid, by direct reaction between sulfur trioxide and nitric oxide or between sulfur dioxide and nitrogen pentoxide, and by reaction between pyrosulfuric acid and nitrogen tetroxide (*19*, *28*, *54*). It is a colorless crystalline compound, melting at 217°C. and boiling at 360°C. without decomposition.

4. Nitrosyl perrhenate, $NOReO_4$, which has been obtained as a colorless, hygroscopic, crystalline powder by passing dry nitric oxide gas into perrhenic acid solution which has been concentrated to just short of separation of rhenium heptoxide (*53*).

5. Nitrosyl thiocyanate, NOSCN, which has been prepared in solution as a blood-red, unstable substance by interaction of nitrous and thiocyanic acids and by reaction between nitrosyl chloride and silver thiocyanate in carbon tetrachloride (*26*, *42*). It can also be obtained by treating thiocyanic acid with ethyl nitrite, but not by interaction of thiocyanogen and nitric oxide (*26*). The pure material has never been isolated.

6. Nitrosyl fluophosphate, $NOPF_6$, nitrosyl fluoarsenate, $NOAsF_6$, and nitrosyl fluoantimonate, $NOSbF_6$, which have all been reported but not extensively studied. The phosphorus derivative is obtained by reaction between phosphorus pentafluoride and nitrosyl fluoride (*25a*), and the other two are obtained by reaction between nitrosyl chloride and arsenic trifluoride and antimony pentafluoride, respectively (*36*).

7. Nitrosyl tetrathiocyanatodiammine chromate (III), $NO[Cr(NH_3)_2(SCN)_4]$, which has been prepared by treatment of the corresponding ammonium compound (Reinecke's salt) with nitric acid or by treatment of an acidified solution of Reinecke's salt with a mixture of nitric oxide and nitrogen dioxide (*49*). It is described as a crystalline compound which appears black in reflected light. In its reactions with water, alkali, and ammonia it is said to resemble nitrosyl sulfuric acid (*49*).

8. Nitrosyl fluosulfonate, $NOSO_3F$, which has been obtained in admixture with about 20 per cent nitrosyl sulfuric acid as a colorless, hygroscopic crystalline material by reaction of nitrogen trioxide with fluosulfonic acid (*25*). This substance is believed to be somewhat analogous to nitrosyl perchlorate (*25*).

SIMPLE COMPOUNDS CONTAINING THE NO^- GROUP

The only reported example of a simple compound containing this grouping is sodium nitrosyl, NaNO. This compound has been obtained by action of dry nitric oxide on sodium dissolved in liquid ammonia (*55*). It is described as a white, rather unstable solid which differs distinctly in chemical properties and in X-ray diffraction pattern from sodium hyponitrite, which has the same stoichiometric composition. On the basis of its diagmagnetic properties it is believed to contain the NO^- ion (*11*). Other highly electropositive metals might be expected to yield similar products.

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Light and Active

ALTHOUGH little known as a war baby, the U. S. production of lithium, lightest of all solid elements, has increased sevenfold during the war. The price of lithium metal, $12.50 per pound in large lots, has not dropped greatly, but some manufacturers predict that, with new production facilities and the hoped-for large postwar demand, a price of $5.00 may be possible.

The justification for lithium's high costs rests on its extraordinary chemical reactivity and on the results obtainable from small quantities. One of its best established uses is in removing by chemical combination (scavenging) the last traces of oxygen and other impurities from high-quality metals and alloys. This ultimate purification often gives surprising results; the electrical conductivity of copper, for instance, is markedly enhanced, and lithium-purified copper is a regular commercial product. The strength and hardness of 6000 pounds of steel can be improved by the "scavenging" effect of one pound of lithium generally contained in a "master alloy" with calcium, copper, or zinc. The internal structure of some metals, including lead, zinc, and aluminum, can be controlled by using small quantities of lithium as an alloying ingredient.

An important wartime product has been a lithium compound which on addition of water releases the hydrogen gas used to inflate balloons for carrying aloft radio atennae and signals from life rafts at sea. A one-pound can of this material, slightly bigger than a tomato can, yields enough gas to inflate the balloon, and five pounds of the compound yield as much hydrogen, 235 cubic feet, as would otherwise be transported under 2500 pounds per square inch pressure in a standard cylinder weighing 140 pounds.

Lithium soaps, the reaction product of lithium and fatty acids from animal and vegetable oils, have been extensively used with lubricating oils to make special lubricants and greases. With lithium soaps added, these greases can maintain the proper viscosity and other physical characteristics at any temperature. As a result they have been especially useful in aircraft lubrication.

The ability of concentrated solutions of lithium chloride or bromide to absorb moisture from the surrounding atmosphere is the basis for their use in air drying, a field in which lithium manufacturers expect an important postwar outlet. In most air-conditioning systems the air is dried by cooling a portion of it more than would otherwise be necessary, so that it cannot hold all the moisture contained in the original fresh air. An alternative method is to cool the air only to the desired temperature and to remove the moisture by passing the air through a spray of moisture-absorbing solution, such as lithium chloride or calcium chloride, or through a solid absorbent, such as silica gel. By this latter means the capacity of refrigeration equipment needed for a given job can be reduced about half, but auxiliary equipment is necessary for heating the absorbent to drive off the moisture so that the absorbent can be used again. For many industrial applications air drying is needed but cooling is not. For such situations, equipment using a lithium absorbent in a compact drying and regeneration cycle is available. Air-conditioning equipment which uses gas flame-absorption refrigeration instead of mechanical refrigeration and which uses a lithium compound as the absorbent has also recently been introduced. This product has been developed for all-year residential and small commercial air-conditioning applications. The same burners are used for heating effect in the winter and cooling in the summer.

Although lithium is not rare, commercial deposits are few and, up to the present, methods of extraction have been difficult and costly. The best sources are in the United States, in the minerals of North Carolina and South Dakota and in the brines of Searles Lake in California. The wartime expansion of production gives lithium producers a real opportunity to develop outlets in postwar markets.—Reprinted from the *Industrial Bulletin* of the Arthur D. Little Company (October, 1945).

Our Contribution to Nomenclature

For the energy associated with nuclear disruption: Atomoclastic Energy. (Or, if you want to be classically technical, Schizatomic Energy.) Need we go into the etymology of these?

How to Solve Problems and Influence Students[1]

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ONE of the more important but exasperating items of a chemistry teacher's job is the task of training students to solve numerical problems involving chemical substances and processes. This paper is a plea for wholehearted adoption of the dimensional method of problem solving which is not only logically sound but eminently practical and worth while.

THE DIMENSIONAL METHOD

The dimensional method consists of solving any given problem "in blank" using only the dimensions or labels associated with the numbers involved, followed by eventual substitution of the numbers where the appropriate labels appear. It presents the following practical and pedagogical advantages:

1. It minimizes opportunities for error in setting up the problem for final numerical solution.
2. By setting up in a single operation all the numerical work required for solution, it eliminates (*a*) algebraic manipulations and (*b*) the computation of intermediate answers, both of which processes are extra opportunities for error and call for time and labor.
3. It automatically sets up the work in the most concise form possible, thus eliminating roundabout methods of solution.
4. The student acquires a more lively awareness of the physical nature of the numbers he uses.
5. He learns to analyze a problem logically rather than to search his memory for a formula into which numbers may be substituted.

To utilize the dimensional method to the fullest extent, it is advisable to tag certain quantities which are usually allowed to go *incognito*, for example,

Molecular weight, which is actually (g. of X)/(mol of X) or (lb. of X)/(lb.-mol of X), etc.
Equivalent weight, which is actually (g. of X)/equivalent.
Weight per cent of X in Y, which is actually (g. of X)/(100 g. of Y) or (lb. of X)/(100 lb. of Y), etc.
Specific gravity, which is actually (density of X)/(standard density of water).

Each of these and other quantities used in chemical problems is a *ratio* of two labels and thus serves to link them together. For example, to get from weight to volume, one should use the conversion factor containing both labels—that is, the density, the ratio of weight to volume. Furthermore, it is immediately obvious *how* to use it. It must be associated with the given weight so that the weight label will cancel out and the volume label will appear in the numerator. Hence, to get volume from weight, one *divides* the weight by the density, obtaining the dimensional identity

$$\text{vol.} = \text{wt.} \div \text{wt./vol.} = \text{wt.} \times \text{vol./wt.} \equiv \text{vol.}$$

Consider the problem, "How many ml. of 0.4 *N* H_2SO_4 will be required to precipitate completely the Ba^{++} in 2.5 g. of $BaCl_2$?" A dimensional analysis of the problem shows:

1. Starting point: g. of $BaCl_2$
2. Goal: ml. of acid solution
3. Conversion factors (connecting links)
   (g. of $BaCl_2$)/(mol of $BaCl_2$) from molecular weight
   (equiv.)/(mol of $BaCl_2$) from valence number of Ba^{++}
   (equiv.)/(liters of acid soln.) from normality
   ml./liters from ratio of units

The dimensional solution of the problem starts by operating on the starting point (g. of $BaCl_2$) by the conversion factor containing this label, *i. e.*, the molecular weight of $BaCl_2$, in such a way as to eliminate the original label. Thus, division of g. of $BaCl_2$ by the molecular weight converts it into mols of $BaCl_2$. Thence it is easy to proceed by obvious steps as indicated below to equivalents, to liters of acid solution, and finally to ml. of acid solution, the required goal:

$$\text{g. } BaCl_2 \times \frac{1}{\frac{\text{g. } BaCl_2}{\text{mol } BaCl_2}} \times \frac{\text{equiv.}}{\text{mol } BaCl_2} \times \frac{1}{\frac{\text{equiv.}}{\text{l. acid soln.}}} \times \frac{\text{ml.}}{\text{l.}} = \text{ml. soln.}$$

If this seems rather complex, let us realize that such a logical analysis *must* be performed, mentally or explicitly, before the problem can be solved. Once performed, mentally or explicitly, it remains only to substitute numerical values:

$$2.5 \times \frac{1}{208} \times 2 \times \frac{1}{0.4} \times 1000 = 60.1 \text{ ml. of } 0.4\ N\ H_2SO_4$$

Compare this method with that actually employed by one student:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

$2.5/208 = x/235$; $x = 2.83$ g. $BaSO_4$
$2.83/235 = x/98$; $x = 1.178$ g. H_2SO_4
0.4 *N* H_2SO_4 contains $0.4 \times 98/2 = 19.6$ g. H_2SO_4/l.
$1.178/19.6 = x/1$; $x = 0.0601$ l. $= 60.1$ ml.

Parenthetically, it may be reported that the student's solution had no labels whatever, leaving it to the instructor to find his way through the problem unaided by guideposts. This student's insistence upon (1) using proportions as a universal tool and (2) computing intermediate answers has led him (*a*) to use an unnecessarily roundabout method which involved setting up and solving three separate equations and (*b*) to

[1] Presented before the Division of Chemical Education at the 109th meeting of the American Chemical Society in Atlantic City, April 8–12, 1946.

ignore the fact that he had put in the molecular weight of H_2SO_4 (as well as that of the quite irrelevant $BaSO_4$) and then taken it out again. Even using his clumsy reasoning, had he not computed intermediate answers, his final computational setup would have shown him the obvious cancellations, eliminating the unnecessary molecular weights,

$$\frac{2.5 \times 235}{208} \times \frac{98}{235} \times \frac{1000}{0.4 \times 98/2} = \frac{2.5 \times 2 \times 1000}{208 \times 0.4}$$

exactly what was obtained by the dimensional method in one step.

Consider a more complex problem: "A solution of Na_2CO_3 (sp. gr. 1.08, 20 per cent by wt. Na_2CO_3) is treated with concentrated hydrochloric acid (sp. gr. 1.20, 39.0 per cent by wt. HCl). What volume of acid would be required to react with 50.0 ml. of the Na_2CO_3 solution and what volume of CO_2, measured at 25°C. and 740 mm. pressure, could be obtained?" The dimensional analysis is:

1. Starting point: ml. of Na_2CO_3 solution
2. Goals: (*a*) ml. of acid and (*b*) liters of CO_2 at given conditions
3. Conversion factors:
   - density of Na_2CO_3 solution/(standard density of H_2O) from sp. gr.
   - g. of H_2O/(ml. of H_2O) from standard density of H_2O
   - g. of Na_2CO_3/(g. of Na_2CO_3 solution) from wt. per cent
   - g. of Na_2CO_3/(mol of Na_2CO_3) from mol. wt.
   - mol of HCl /(mol of Na_2CO_3) from chemical equation
   - g. of HCl/(mol of HCl) from mol. wt.
   - g. of HCl/(g. of acid) from wt. per cent
   - density of acid/(standard density of H_2O) from sp. gr.
   - mol of CO_2/(mol of Na_2CO_3) from chemical equation
   - liters of CO_2 at S.T.P./(mol of CO_2) ideal gas molar volume.

Solution:

(*a*) $$50 \times 1.08 \times 1.00 \times 0.20 \times \frac{1}{106} \times 2 \times 36.5 \times \frac{1}{0.390} \times \frac{1}{1.20} = 15.9 \text{ ml. acid soln.}$$

(*b*) $$50 \times 1.08 \times 1.00 \times 0.20 \times \frac{1}{106} \times 1 \times 22.4 \times \frac{760}{740} \times \frac{298}{273} = 2.48 \text{ l. } CO_2 \text{ at given conditions}$$

In each case the relevant factors are used in the order listed. The technique of the conversion of gas volumes is discussed below. As in the previous problem, dimensional analysis leads directly to the *simplest possible formulation* ready for immediate computation without further algebraic manipulation.

It is, of course, obvious that familiarity with dimensional analysis and experience in working problems—experience which the teacher possesses and the student lacks—make possible certain short cuts in method. For example, dragging in the dimensions of specific gravity and multiplying by the unit density of water seem rather pedantic. However, consider the simple problem, "What is the weight in lb. of a gallon of sulfuric acid of specific gravity 1.632?" In this case a thoughtless interpretation of specific gravity as numerically equal to density would give a very erroneous result, whereas actually

$$\text{sp. gr.} = 1.632 \frac{\text{lb./gal. of acid}}{\text{lb./gal. of } H_2O}$$

and must be multiplied by 8.33 lb./gal. of H_2O before a quantity with the required label "lb. acid/gal. acid" is obtained. The proper solution is, of course,

$$1 \times 1.632 \times 8.33 = 13.59 \text{ lb. acid}$$

GENERAL AND SPECIFIC LABELS

To the physicist, specific gravity is "dimensionless" because he is usually uninterested in chemical reactions or the chemical nature of the objects he handles. He uses *general* labels—for example, "grams" rather than "grams of water," or "sq. ft." rather than "sq. ft. of wall." To the physicist, therefore, specific gravity is simply density/density, *i. e.*, a pure number.

To the chemist, however, the nature of the material is frequently all-important, especially if one kind of matter is being transformed into another. The chemist uses labels specifying the chemical substance involved, and to him specific gravity is, or should be, (density of X)/(standard density of H_2O), a ratio of two *different* labels and thus not a dimensionless quantity.

Specific labels help to avoid the common student error of using just "g." as a label, meaning "g. of X," and then substituting this number where "g. of Y" should have been used. We teachers should insist (1) that all answers be labeled and (2) that all labels should be specific.

THE UBIQUITOUS PROPORTION

The dimensional attack largely bypasses the exaggerated use of proportions. Almost always the use of proportions, while not wrong, is clumsy and wasteful of time and effort. It is usually simpler and more expeditious to avoid them. For example, in the usual gas law problem, such as "What volume will be occupied at S.T.P. by 250 ml. of gas measured at 750 mm. and 30°C.?," instead of explicitly recalling that "volume at constant temperature is inversely proportional to pressure" and writing

$$v/250 = 750/760$$

$$v = 250 \times 750/760$$

followed by recalling explicitly that "volume at constant pressure is directly proportional to absolute temperature" and writing

$$\frac{v}{250 \times \frac{750}{760}} = \frac{273}{303}$$

$$v = 250 \times \frac{750}{760} \times \frac{273}{303}$$

it is far simpler to write at once

$$\text{new vol.} = \text{old vol.} \times \text{ratio of pressures} \times \text{ratio of temperatures}$$

or

$$v = 250 \times (\text{press./press.}) \times (\text{temp./temp.})$$

It is always intuitively obvious which pressure and

temperature to put on top in the ratios; in the present instance, the lower pressure (because going from low to high pressure will obviously *reduce* the volume) and the lower temperature (because cooling the gas will obviously cause it to *contract*). Hence,

$$v = 250 \times (750/760) \times (273/303)$$

exactly the solution arrived at more laboriously by proportions.

Another minor count in the indictment against the use of proportions always and forever is based upon the curiously inflexible pattern of solving a proportion by cross multiplying. For some reason, given the proportion

$$v/250 = 750/760$$

it seems to be the rare student to whom it occurs to solve the equation for v by the simple process of multiplying through by 250. Instead, experience indicates that more than half will first write

$$760\,v = 750 \times 250$$

and subsequently divided by 760, making two bites to a cherry. Probably the mathematicians have taught too well that in any proportion the product of the means equals the product of the extremes. Possibly if the student could be made to recognize the original equation as simply an algebraic equation in one unknown, v, rather than as a proportion, he might solve for v directly.

This seems a good point at which to repeat that it is much better to reserve computation until the problem is essentially completely solved, particularly if a slide rule or a table of logarithms is to be used. Computation of intermediate answers frequently obscures simplifying cancellations, as was illustrated above in the student's solution to a problem.

In conclusion, I should like to advocate strongly as a standard practice adequate drill, not only in obtaining numerical answers to a problem but also in formulating the solution according to a logical dimensional pattern. Further, we should emphatically insist upon a *specific* label to every answer.

Objective Tests in Organic Chemistry

THE NATION has been working harder than at any time in its history, yet it is not necessary for one to slave at a testing program in organic chemistry. Seven complete sets of objective tests in organic chemistry are now available. These comprise the series from 1940–1941 to 1946–1947, inclusive.

Each of these series contains 27 subject examinations on the various topics of organic chemistry as:

1. Alkanes, alkenes, alkynes.
2. Alkyl halides and polyhaloalkanes.
3. Alcohols, ethers, halohydrins, alkene oxides.
4. Aldehydes, ketones, ketenes.
5. Acids, saturated and unsaturated.
6. Halogen, hydroxy, and oxo-substituted acids.
7. Anhydrides, acid halides, esters, salts.
8. Replacement reactions, review.
9. Carbohydrates.
10. Final examinations, Nos. 1 to 9.
11. Thioalcohols, thioethers, sulfonic acids.
12. Nitroparaffins, amides, urea, urea derivatives, amines amino acids, proteins, nitriles, and isonitriles.
13. Foods and metabolism.
14. Metallic and nonmetallic alkyl compounds.
15. Alicyclic compounds.
16. Aromatic hydrocarbons.
17. Aryl halogen compounds.
18. Phenols, aryl alcohols, ethers.
19. Aryl aldehydes, ketones, quinones.
20. Aryl carboxylic acids.
21. Aryl sulfonic acids.
22. Aryl nitro compounds, amines, and diazonium salts.
23. Heterocyclic and miscellaneous compounds.
24. Antiseptics, dyes, stains, indicators.
25. Terpenes, rubber, resins, fibers, and detergents.
26. Processes, reactions, syntheses, tests.
27. Final examinations, Nos. 11 to 26.

Each test contains 20 items of the multiple choice type, in which zero to five answers may be correct. Both individua answers and various combinations of answers are employed.

The completion time of each test is 20 or more minutes. The instructor may, however, select only such items as he desires to emphasize and thus cut the test to a 10- or even a 5-minute quiz.

These five series of tests have been compiled and edited by a volunteer group of collaborators. As a consequence it is likely that the tests are representative.

These tests may be used advantageously with any textbook in any course in organic chemistry, for the individual tests cover specific areas of the subject.

The tests are so arranged that they may be graded manually, by cutting out small rectangles below the answers on a master key, and then superimposing the key on the test paper to be graded. Where machine grading is available, the numbering of the items is such that two answer sheets are all that are required for a complete course in organic chemistry.

These subject tests are available at 60 cents for the first set and 20 cents per set for each additional set, approximately 20 cents per student per year, plus postage. Individual sets are priced at 60 cents. All orders for less than $2.00 should be accompanied by payment. These tests are available from the chairman of the committee, Ed. F. Degering, Department of Chemistry, Purdue University, Lafayette, Indiana.

This is a nonprofit project, which has been subsidized by Purdue University from the outset.

Three comprehensive objective tests in organic chemistry are also available, Form S, Form T, Form U, and Form W. These are obtainable from the Cooperative Test Service, 15 Amsterdam Avenue, New York, New York.

These comprehensive tests contain 100 carefully selected items each, which give a representative coverage of a beginning course in organic chemistry. One hundred minutes are required for the completion of each of these examinatons, but Forms T and U are so designed that they may be given in two 50-minute periods.

Cooperation in the production of subsequent sets of both of these series of tests is cordially invited.

Particle Size Determination

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IN THE teaching of chemistry it is often necessary to refer to the particle size of finely divided materials, but the student rarely has a very clear idea of how such sizes are determined. The purpose of this paper is to present a short summary of the methods for determining particle size in the subsieve range without attempting to make a critical survey of the limitations of the various methods. Excellent reviews and summaries of references have been given by Schweyer and Work[1] and by Schuhman.[2]

In dealing with a large amount of a powder it is rarely possible to determine each individual particle size. Rather it is necessary to determine the particle size distribution—that is, the way in which the particles are distributed among the various sizes measured. The meaning of the term "particle size" is itself difficult to establish and depends to some extent upon the method of measurement. When the size is measured by a microscope, the result is the average of the dimensions of the particle; when a sieve is used, the particle size is designated as a dimension of the sieve opening which just retains the particle; when sedimentation is used, the size is the diameter of a sphere which has the same density and rate of settling as the actual particle measured.

Sieves are made with meshes of varying sizes so that powder can be separated into fractions which will pass through one sieve but not through the next smaller one. In most cases the smallest particle size which can be measured reliably by a sieve is 44 microns—this being the size of the opening in a 325-mesh wire; the determination of the size of particles smaller than 44 microns is the main interest of this paper.

Since the methods which depend upon sedimentation are more numerous than any other, they will be discussed first. The particular sedimentation method used depends upon the particle size range to be measured, the nature of the material, the time and facilities available, and whether it is desired to determine the size range only or also to fractionate the material. The methods which are not based upon the rate of settling of the particles are equally important but, in general, have specialized applications.

[1] SCHWEYER, H. E., AND L. T. WORK, Symposium on "New methods for particle size determination in the subsieve range," A.S.T.M., March 4, 1941.

[2] SCHUHMAN, R., JR., in J. Wolff, "Powder Metallurgy," American Society for Testing Materials, Philadelphia, 1942, Chapter 17.

SEDIMENTATION METHODS

Theory. All sedimentation methods make use of the principle that the rate at which a particle settles in a fluid is related to the size of the particle. Many times the relation is empirical, but ideally the rate of settling is defined by Stokes' law,

$$v = \frac{g(D_p - D_M)d^2}{18\,N \times 10^3}$$

where v = the terminal velocity or velocity at the point at which the particle size measurement is made (cm. per sec.), g = acceleration due to gravity (cm. per sec. per sec.), D_p = the density of particle (grams per ml.), D_M = the density of suspension medium (grams per ml.), d = the diameter of spherical particle (microns), and N = the viscosity of the dispersion medium (poises). As pointed out earlier, the size of an irregularly shaped particle is described as the diameter of a sphere which will settle at the same rate as the particle to be measured.

A summary of the conditions which must be established for accurate application of Stokes' law has been given by Schuhman.[2] These will not be discussed here but it is well to remember that each method of particle size determination has its limitations, which usually depend upon the particle size being measured.

Fractionation Methods. If it is desired to separate the material into fractions which have a certain desired particle size range, there are several methods available.

Decantation: One of the simplest fractionation methods is to make a suspension in a beaker, allow settling to take place for a predetermined time, t, and siphon off to a known depth, S. The beaker will then contain all the particles which have settling velocities greater than S/t and some with velocities less than the value; if more water is added and the procedure repeated several times, practically all the particles smaller than those with a settling velocity S/t will have been removed. The decanted solvent is evaporated, the weight of suspended material determined, and the fraction of the original material which contains particles with a settling velocity less than S/t calculated. By adjusting the time and height, any desired size analysis can be made.

Elutriation: The principle of elutriation methods is that particles are caused to settle vertically against an upward moving stream of water or air; particles with settling velocities less than the upward velocity of the

air or water will be carried away. Since the net upward velocity of the particle will be the difference between the upward velocity of the fluid and the downward settling velocity of the particle, good recovery of particles near the limiting size requires much time. Elutriators using air or water are composed of a series of chambers of increasing size in which the upward velocity of the fluid decreases in steps; thus the particles collecting in each chamber will be in a different size range. If the application of Stokes' law is not exact, a size range which is collected in each chamber may be established empirically.

Nonfractionation Methods. The principle of all nonfractionation methods is that a suspension is allowed to settle under set conditions, and measurements are made at certain depths after certain settling times.

Pipet Method: In this method a suspension of a known amount of material is allowed to settle for a time, t, and a known volume of fluid is removed from a known depth, S, by a pipet. The solid content of the removed suspension will be composed of particles with a settling velocity less than S/t; after evaporation of the dispersion medium of the removed sample, the weight fraction of the original solid, which is composed of particles with a settling velocity less than S/t, can be determined. By use of the Stokes equation the diameter of particles which correspond to a settling velocity of S/t can be calculated; then the fraction with particle sizes less than the value has been established.

Andreason[3] has designed a simple, adaptable, and rapid pipet apparatus which is available from commercial sources.

Hydrometer Method: Bouyoucos[4] and Casagrande[5] have developed a widely used method which uses a hydrometer to measure the concentration of suspended material at a known distance below the surface of the suspension. The hydrometer measures the density at a point which is called the center of volume of the instrument. It is possible to calculate the distance between the center of volume of the hydrometer and the surface of the suspension for any hydrometer, but it is preferable to use special hydrometers which either give direct reading of this distance or have markings from which it can be calculated. The relation between the amount of suspended material and the density is obtained as follows: Let W = the weight of particles in suspension. They have not settled and therefore have diameters of d or smaller. V = the volume of suspension. Then W/V = the weight of solid per unit volume at height, H, and after time, t. The volume of liquid displaced is

$$W/D_pV$$

where D_p is the density of the particles. The weight of the liquid per unit volume of suspension is

$$D_m\left(1 - \frac{W}{D_pV}\right)$$

where D_m is the density of the dispersion medium. The specific gravity of the suspension, R, is given by

$$R = W/V + D_m\left(1 - \frac{W}{D_pV}\right)$$
$$= D_m + \left(\frac{D_p - D_m}{D_p}\right)\frac{W}{V}$$

and

$$W = (R - D_m)\left(\frac{D_p}{D_p - D_m}\right)V$$

The per cent of material which has not settled is then

$$\text{per cent } W = 100\,\frac{W}{W_0} = \frac{100}{W_0}(R - D_m)\left(\frac{D_p}{D_p - D_m}\right)V$$

where W_0 is the weight of the original suspension in volume V. The weight of suspended material calculated from hydrometer measurements after a given settling time, t, is the weight of the particles with settling velocities less than S/t where S is the distance from the suspension surface to the center of volume of the hydrometer. Using Stokes' law as before, the diameters of the particles which have settling times less than S/t can be calculated. A series of measurements at various times will give a size distribution of the suspended particles.

The hydrometer method is simple and rapid but careful attention must be given to the technique necessary for accurate measurements.

Sedimentation Balance: Much work has been done to develop a method to measure the amount of settled material by an analytical balance. One balance pan is suspended in a dispersion at a known distance from the surface, and at desired settling times the weight of the sediment is determined. It is claimed that, if errors due to convection currents are eliminated, a precision of 0.1 per cent can be obtained, compared with an accuracy of 0.5 to 2 per cent for other sedimentation methods. In addition it has been possible to develop automatic recording of the balance measurements.

Turbidimetric Methods: The scattering and transmission of a beam of light passed through a suspension will depend, other things being equal, upon the surface area of the suspended particles. This principle has been adapted to measurement at a given point in a suspension if the particles are settling according to Stokes' law. A glass cell containing the suspension is supported between a light source and a photocell. The transmitted light intensity, which is recorded by the photo-cell, is related to surface area of suspended particles by the equation,

$$A = k \log \frac{I_0}{I_t}$$

where A = surface area of particles in the path of the light beam, k = a constant, I_0 = intensity of the incident light, and I_t = intensity of the transmitted light.

The measurements of the intensity of transmitted light must then be converted into particle size ranges by a fairly long mathematical integration. Sufficient work has been done with the method to show that there are many precautions which must be taken in interpreting the results, but in its favor is the fact that the turbidi-

[3] ANDREASON, A. H. M., *Kolloid-Beihefte*, **27**, 349 (1928).
[4] BOUYOUCOS, G. J., *Soil Sci.*, **23**, 343 (1937).
[5] CASAGRANDE, A., "The Hydrometer Method for Mechanical Analysis of Soils and Other Granular Materials," Soil Mechanics Laboratory, Massachusetts Institute of Technology, 1931.

metric method is rapid and useful for comparative measurements.

CENTRIFUGING

Any method of particle size analysis which depends upon gravity settling is limited to determination of particle sizes larger than one micron. When the particle sizes are smaller than this value, the buoyant force approaches the gravity pull with the result that separation is very time-consuming, if not impossible. Svedberg devised a modified form of Stokes' equation which can be used in the analysis of a suspension which has been rotated in a centrifuge. This equation is

$$t = \frac{n \log \frac{R_2}{R_1}}{3.81\ N^2 r^2\ (D_1 - D_2)}$$

where N = revolutions per second, r = the radius of the particle, D_1 and D_2 = the density of the particle and medium, respectively, R_1 and R_2 = the distance from the axis of rotation to the surface of suspension and to the sampling depth, respectively, t = time, and n = the viscosity of the medium.

In centrifugal analysis the suspension is rotated for a known time, and the solid content at a known distance from the liquid surface is determined by some convenient method. The size of particles which have not settled past the measurement point can be calculated from Svedberg's equation, and then the per cent with sizes equal to or smaller than this value can be established. Ordinary centrifuges are useful for analysis of particles between 10 microns and 0.05 micron in diameter; supercentrifuge and ultracentrifuge methods have been developed for very small particle size separations.

MICROSCOPIC METHODS

Determination of particle size distribution with an optical microscope is too tedious to be used in much routine work; it is, however, the most accurate way to check on particle size measurements made by any other method. A drop of suspension is placed on a microscope slide and focused in a microscope; the field and micron scale are then projected on a screen which is marked in squares in order to make it easier to keep a record of the part counted. The sizes of all the particles in each square are obtained by comparison with the projected scale, and the results are tabulated.

The electron microscope has made possible the measurement of particle size down to 0.01 micron. A picture of the particles is obtained in a photographic print and the sizes of the images of the various particles are measured directly; then using the magnification factor, the actual sizes of the particles can be calculated and a size distribution made.

SURFACE AREA

After a particle size distribution of a powder has been obtained, it is frequently desirable to know the total surface area. Such information can be calculated assuming the particles are spheres, but considerable error is introduced in so doing. The adsorption of nitrogen and argon at temperatures near their boiling points has been used by Emmett[6] and Harkins[7] to measure total surface area without regard to particle shape.

A plot is made of volume of nitrogen adsorbed against pressure, and the point is selected which corresponds to a mono-molecular layer of absorbed gas. From the mono-layer adsorption volume the number of molecules can be calculated, and when this number is multiplied by the average area covered by a molecule, the total surface area is obtained. Much research has been done on the experimental technique and theoretical analysis with the result that the method has become very practical.

[6] EMMETT, P. H., Symposium on "New methods of particle size determination in the subsieve range." A.S.T.M., March 4, 1941.

[7] HARKINS, W. D., Conference on "Catalysis" of the American Association for the Advancement of Science at Gibson Island, Maryland, June 11, 1945; *Science*, 102, 263 (1945).

Progress in Science

"Where one man fails in an experiment, another succeeds. What is unknown in one age is clarified in the next. The arts and sciences are not cast from a mold: they are shaped and polished little by little, here a dab and there a pat—as bears leisurely lick their cubs into shape. What my powers cannot solve I still persist in sounding and trying out. By kneading and working over the new material, turning and warming it, I make it more supple and easier to handle for the man who will take it up after me. And he will do as much for a third. This is why I should not despair of difficulties or of my own incapacity—for it is only my own."

This marvelous word-picture of progress in the sciences and the arts, written back in the 16th century by Michel de Montaigne, is as modern as today's newspaper headlines—which is characteristic of so much that this amazing man wrote. And his reminds us to suggest, if you are seeking some really enjoyable reading, that you look up The Autobiography of Michel de Montaigne, by Marvin Lowenthal. It is a book that will repay reading—and rereading.—From The Research Viewpoint.

Max Abramovich Blokh

His Contributions to the History of Chemistry

HERBERT S. KLICKSTEIN[1] AND HENRY M. LEICESTER

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THERE is in Russia a deep interest in the relationship of science and literature and in the history of science. In large measure this historical interest seems to be characteristic of Russian scientists, for even before the revolution a large amount of excellent historical and biographical material appeared in the Russian literature. This natural interest has been stimulated since the revolution by certain aspects of Marxist philosophy. Karl Marx defined the nature of the culture of any period as based on the system of contemporary social production; thus, the Marxist seeks relations between science and the mode of production at any period. The correlation of the social environment and the various sciences is also explored. This principle of Marx has encouraged historical research in the Soviet Union from a new point of view and has been responsible for state support and encouragement of historical studies. As a result, many institutions have turned their attention to such studies. The University of Moscow has a department of the history of sciences, and the Academy of Sciences, the Physical Institute in Moscow, the Gertsen Institute, and others have special chairs for research in the history of science. Many remarkable studies have appeared, some of which have been reviewed by Crowther.[2]

The reasons for the lack of information on Russian activities in this field among scientists outside the Soviet Union are clear. The difficulty of reading the Russian language and the limited circulation of Soviet scientific periodicals and books account for our failure to recognize many of their contributions, and this is especially true of works on the history of chemistry. Few studies have been made in this direction. The work of Davis[3] brought out clearly the excellent historical work of B. N. Menshutkin[4] who contributed so much of value to future students. Another Russian chemical historian, as great but less well known, is Max Abramovich Blokh.

Blokh was born on August 16, 1882.[5] He received his elementary education in Dvinsk and then attended the Riga Polytechnic Institute, where he studied chemistry under Walden[6] and received his degree with distinction in 1903. Blokh then went to Germany for graduate work, and in 1904–05 he studied at Heidelberg under Bredig,[7] Curtius,[8] and Jannasch.[9] Most of his time was spent with Bredig, in whose work he found much of interest. This interest never left him, and in later years he wrote a series of monographs on problems of solutions and catalysis.

Even as a student at Riga, Blokh clearly showed his interest in the history of science. In his first year he prepared a sketch on the history of the theory of electricity which was afterwards accepted for publication. This was followed by a paper on the history of quantitative volumetric analysis.

When his studies at Heidelberg were completed, Blokh returned to Riga but was unable to obtain a state position because of his Jewish birth. Professor O. O. Lutz of the Walden Laboratory invited him to act as his private assistant, and Blokh accepted. He worked in the field of inorganic and analytical chemistry. He studied a new modification of sulfur, investigated the sensitivity of the known methods for determining copper, and devised an apparatus for the determination of nitric acid. At the conclusion of these studies, Blokh turned from experimental work and devoted his time entirely to studies in the history of chemistry and to the organization of the publication of scientific books and journals.

His activities in the field of publication began in 1916 when he organized a bureau which issued a Bulletin of Statistical Information, a project of great value to chemists and chemical engineers. At the same time he conceived the idea of publishing a new journal to acquaint chemists with the economic and technical aspects of their science. These ideas did not reach their full development until after the revolution, however. In 1917 he was given the opportunity to work out his ideas, and he soon founded the first Soviet scientific press, the Scientific Chemico-Technical Press (N. Kh.

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[2] CROWTHER, J. G., "Soviet Science," Kegan Paul, Trench Trubner and Company, Ltd., London, 1936.

[3] DAVIS, T. L., J. CHEM. EDUC., 15, 203 (1938).

[4] Boris N. Menshutkin (1874–1938) was the son of Nikolai Alexandrovich Menshutkin (1842–1907) who was also noted for historical studies. He worked in the fields of physical and organic chemistry and with molecular compounds. He is best known for his historical studies, especially on Lomonosov.

[5] KHLOPIN, V. G., *Uspekhi Khim.*, 10, 501 (1941).

[6] Paul Walden (1863–), professor of chemistry at Odessa, Riga, St. Petersburg, and Rostock. He is noted for his work in organic and physical chemistry and for his studies in chemical history.

[7] Georg Bredig (1868–) studied under Ostwald and received his degree at Leipzig in 1894. He taught at Karlsruhe and Heidelberg and studied ionization constants of weak acids, amphoteric electrolytes, and catalytic reactions.

[8] Theodore Curtius (1857–1928), professor at Kiel, Bonn, and Heidelberg, worked on glycollic esters and polypeptides, and discovered diazoacetic ester, hydrazine, hydrazoic acid, and many heterocyclic nitrogen compounds.

[9] Paul Jannasch (1841–1912), professor of analytical chemistry at Heidelberg.

T. I.). This press existed under various names until 1938 and contributed much to the development of Soviet chemistry.

Under the guidance of Blokh many younger chemists were trained for editorial and publishing positions. He became completely absorbed in the task of creating a new chemical literature for his country. Reference books, either reprints or translations, abstracts, reports on the progress of various branches of science, monographs, and the proceedings of scientific societies appeared under his editorship. One of the most important of these was the *Communications of Scientific Technical Work in the Republic*, the first abstracting organ in the Soviet Union. In addition Blokh published collections of the works of great Russian chemists, such as Mendeleeff, Favorskii, Kurnakov, and Bakh, and issued a series of reprints of chemical classics similar to the *Alembic Club Reprints* or Ostwald's *Klassiker*. Blokh was also active in the organization of research and served on committees to coordinate the relations of the government and the research organizations.

Although it was almost unknown in other countries, Blokh's work on the history of chemistry was recognized throughout the Soviet Union. He was constantly consulted on questions concerning the historical background of the science, and from the beginning he was active in the work of the Commission on the History of Knowledge of the Academy of Sciences. To him was entrusted the task of publishing the scientific works of Mendeleeff.

He was also active in teaching after 1917. He organized the chemical department of the Pedagogical Institute in 1919 and gave special courses at the Chemico-Pharmaceutical Institute and the Kirov Industrial Academy in Leningrad. His most valuable and important courses were those on the history of chemistry and the chemical industry. The work of students in chemical history in the Gertsen Pedagogical Institute was under his guidance. Here diplomas were given for all levels of study in the history of chemistry. A chair of the history of chemistry such as Blokh occupied could profitably be established in our universities.

A complete examination of all of Blokh's historical publications is beyond the scope of this paper,[10] but a general survey of his work will show the extent of his contributions. His studies in the history of chemistry can be divided into three classes: (1) reference works for research in chemical history; (2) monographs on the history of chemical ideas and their creators; and (3) specialized papers on the history of chemistry and chemical industries.

To the first group belong his two principal works, "Biographical References to Outstanding Chemists and Scholars of the Nineteenth and Twentieth Centuries Who Worked in Fields Relating to Chemistry," two volumes of 837 pages, published by N. Kh. T. I. in 1929–30, and "Chronology of the Most Important Events in the Field of Chemistry with a Bibliography of the History of Chemistry and Related Sciences," published by the State Scientific Technical Press in 1940. The first of these publications includes not only biographical data on chemists, but also information on specialists in nearby fields. Many nearly forgotten workers are described in this book.

The scope and amount of material included in the second work is truly gigantic. It is difficult to realize that one man could produce such a study. The chronology itself comprises 382 pages and extends from prehistoric times to 1900, including over 7000 dates. This is followed by a literature survey to 1936 of 255 pages and over 15,000 references. A supplementary survey at the end of the book carries the literature to 1940. Following the literature references come lists of histories of chemistry, jubilee publications, histories of chemical industry, physics, technology, biographies, chronologies, histories of scientific institutions, general works, bibliographies, and addresses of publishers and journals which publish historical material. Although these lists are not exhaustive, they are a guide to much material which could easily be overlooked. The work concludes with name and subject indexes to the chronology and a short subject index to the literature.

In the introduction Blokh points out that a history of the material basis of society in the Marxian sense has not yet been written, and he has compiled the chronology "to make a small contribution to the preparation of this work." He rightly points out that his book is solely a reference work and then goes on to describe his own efforts in writing it:

> As a young student the author began the study of the original sources in the history of chemistry and not once did he interrupt this work over a long period of time. During the years of study, as the work itself grew, the learning of the author deepened, and much which he once wrote, he would now handle in a different way. The decision of the author to publish part of his work was due to the fact that neither in the Russian nor the world literature on chemistry was such a chronological summary known.

The chief weakness of the work lies in the form of the references, which is not uniform. Often not enough information is given to permit ready location of the desired article without a prolonged search. This carelessness is difficult to understand, but the fault is overshadowed by the magnitude of the work and by the coverage in great detail of the Russian literature. It is probable that nowhere else is such a complete list of obscure articles to be found.

The second group of publications by Blokh comprises some 32 monographs on outstanding chemists and the evolution of chemical ideas. His works on the era of Van't Hoff, Arrhenius, and Ostwald contain much valuable material. Studies of Lunge, Planck, Avogadro, Gay-Lussac, Gehardt, Laurent, and others were also published, some of them in German.

The third group contains 39 papers on special topics in chemical history. It also includes a series of translations edited by Blokh, and in some cases the introductions are practically new books in themselves.

[10] A critical analysis of Blokh's major historical contributions will be made in a later paper.

Although Blokh closed his chronology with the hope that he might publish a "synthetic development of the basic ideas of chemistry, not in the form of a dry chronological table, but as a coordinated report," he was unable to fulfill this promise, for he became ill and died on January 11, 1941. He left behind in manuscript form much rich material on Lavoisier, the history of the theory of solutions, lectures on the history of chemistry, and a history of chemistry for children.

The following bibliography of the publications of Blokh on the subject of the history of chemistry is drawn from the index to his chronology. It has been arranged chronologically, and the incompleteness of the references in many cases is an illustration of the carelessness with which they are given in the original. The bibliography also indicates the many obscure items which would be very difficult to locate in any conventional index.

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Ion Exchange*

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A CENTURY ago J. T. Way (*25*), consulting chemist to the Royal Agricultural Society of England, wanted to know why water-soluble fertilizers like ammonium sulfate or potassium chloride stayed in the soil and did not wash out when it rained. He put some soil in a vertical cylinder with an outlet at the bottom and poured over it a solution of ammonium sulfate, washing down with water. In the liquid that drained out of the bottom he found no ammonium salts, no matter how much wash water he used, but instead, the first portions of liquid to come out contained calcium sulfate. If he poured potassium chloride in at the top, calcium chloride came out of the bottom; sodium nitrate poured in gave calcium nitrate coming out; in every case, the "base," or positive radical, was retained by the soil, while the "acid," or negative radical, went through unaltered. This was the first recorded case of "ion exchange." Way's discovery was an example of "cation exchange," or "base exchange," as he called it. "Anion exchange," in which dissolved anions are exchanged for other anions by contact with a solid body, is also known, and indeed takes place in the soil to some extent. A great variety of substances, natural and artificial, organic and inorganic, are now known which have the property of ion exchange, and many important uses have been found for this phenomenon.

An ion exchanger is an insoluble solid which is at the same time a salt, acid, or base—that is to say, it must have ions of its own to exchange for others. Furthermore, it must have a highly porous structure or else a very large exposed surface to permit these ions to get in and out. These characteristics are found in the zeolite minerals. Indeed, at one time the zeolites were so closely identified with ion exchange that the term "zeolite" was extended to include all ion exchanging substances. This usage persists today, except for the organic exchangers, and the ion exchange process for softening hard water is usually called the "zeolite process" even though true zeolites are never used for this purpose. An example of a true zeolite is natrolite, $Na_2Al_2Si_3O_{10}$. The negative ions of natrolite are not single $Al_2Si_3O_{10}$ groups, but an endless three-dimensional framework in which this unit of two Al, three Si, and ten O atoms occurs repeatedly, like the pattern on wallpaper. Two out of every ten oxygen atoms bear a negative charge. This particular framework has three sets of parallel channels at right angles to each other, running through the whole crystal; the sodium ions reside in these channels, their positive charges exactly neutralizing the fixed negative charges of the aluminosilicate framework (*15*). Because of the channeled structure the sodium ions can easily move out, but when they do move out, other positively charged ions must move in to take their place, or the negative charges of the framework will not be neutralized. A potassium ion can move in and displace a sodium ion, or a calcium ion with its double charge can displace two sodium ions. This is the process of ion exchange.

The clay minerals show ion exchange too because besides being salts (or weak acids, like kaolinite, $H[AlSiO_4] \cdot H_2O$) they are made up of very thin plate-like crystals, and a large proportion of their ions are on the surface (*8*). The humic acids of the soil have a rather similar form and show ion exchange for the same reason. Both clay and humus give cation exchange to soils, as Way recognized, and help the soil to retain fertilizers.

A typical synthetic ion exchanger (a so-called "synthetic zeolite") is the sodium aluminosilicate used in water softening. This is made by mixing solutions of sodium silicate and sodium aluminate; immediately after mixing, the liquid sets to a stiff gel which is over 90 per cent water and very porous. The gel is broken up, washed, and dried; during drying it shrinks considerably, but still retains a very porous structure, far more porous than the natural zeolites. Its chemical formula is approximately

$$Na^+[AlSi_3O_8]^-$$

and the sodium, being ionic, can be replaced by other cations. The formula is the same as that of the feldspar, albite; yet the latter is a hard, crystalline, impervious rock, showing little or no ion exchange because its sodium ions are imprisoned and cannot get out. In the ion exchanger we have an amorphous, open structure, a continuous but irregular framework of oxygen, silicon, and aluminum atoms, with on the average one negative charge to eight oxygen atoms. A grain of the exchanger, magnified sufficiently, would resemble a sponge whose walls were studded at intervals with fixed negative charges. To balance these charges, positive sodium ions hover in the internal passages and around the surface of the sponge. Suppose grains of this exchanger are placed in a solution of calcium chloride; calcium ions can enter and diffuse right through the grains, but for every calcium ion that enters a grain, two sodium ions must leave to preserve electrical neutrality. The exchanger does not mind very much what particular kind of positive ions it has in its channels, so long as the positive charges always exactly balance the fixed negative charges of the exchanger. In other words, ion exchange always proceeds by equivalents.

* This is adapted from a paper, "Ion exchange phenomena," presented at the Fiftieth Anniversary Meeting of the Chicago Section of the American Chemical Society, held at Northwestern Technological Institute, November 16, 1945.

Ion exchange is a typical reversible reaction. The exchange of calcium for sodium ions can be represented by the equation

$$Ca^{++} + 2(Na^{+}Ex^{-}) \rightleftharpoons 2Na^{+} + (Ca^{++}Ex_2^{-})$$

and the equilibrium obeys the mass-action law:

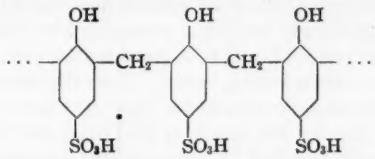
$$\frac{[Na^{+}]^2 \text{ solution } [Ca^{++}] \text{ exchanger}}{[Ca^{++}] \text{ sclution } [Na^{+}]^2 \text{ exchanger}} = \text{a constant}$$

The quantities in square brackets are activities rather than concentrations, although the molar concentrations in the exchanger can be introduced without much error. The equilibrium constant depends on the exchanger, being about 3 for a particular exchanger studied by the author (*24*)—that is to say, the exchanger prefers calcium ions to sodium ions, other things being equal, but not by much. In general, the higher the valence of an ion and the less hydrated it is in solution, the more the ion is attracted to an exchanger (*10*, *23*). Correlations between equilibrium constant and ionic radius have also been noted; up to a point, the larger the unsolvated ion, the better it is held by an exchanger (*10*). Temperature has very little influence on the equilibrium, showing that there is very little heat of reaction in ion exchange (*6*). Ion exchange can be a very fast process, but, of course, the speed of exchange depends greatly on the porosity of the exchanger. For a porous, rapidly acting exchanger, temperature has little or no effect on the speed of exchange, showing that no great energy of activation is needed (*14*). All these facts are in harmony with the picture of ion exchange given in the last paragraph.

The nature of ion exchange can be seen very well in water softening which is the most important technical application of ion exchange and until recently the only one. Hard water, containing harmful calcium and magnesium ions, is allowed to flow down through a bed of cation-exchanger granules containing sodium ions. Calcium and magnesium ions enter the granules and release sodium ions. This exchange is not complete in the top layers of the bed since ion exchange is a reversible process, but as the water, with its calcium partly replaced by sodium, travels down the bed, it is constantly meeting fresh exchanger containing no cations but sodium. The excess of sodium ions forces the equilibrium constantly to the right, and when the water comes out of the bottom of the bed, its calcium and magnesium content is undetectably small. These ions have been replaced by sodium which is not harmful as it does not form a curd with soap nor form scale in steam boilers.

When the bed has taken up as much calcium and magnesium as it can hold and the effluent water is no longer soft, the bed is "regenerated" by flushing it with an excess of concentrated salt brine. About ten minutes' contact is usually sufficient; the excess of sodium ions forces the equilibrium to the left (it is worth noting that the increased *concentration* will displace this equilibrium to the left also), all the calcium and magnesium ions are removed from the bed, and after a rinse, the bed is ready to soften more water. In industrial water-softening installations ion exchangers have been through thousands of cycles of this kind without any deterioration. Because the process is so simple, it is used for softening water at remote railroad stations as well as for big city supplies (*12*), and it is used in homes.

In recent years there have been new applications of ion exchange which have been made possible through the development of new ion exchange materials. Until about ten years ago the only ion exchangers in use were the synthetic aluminosilicates already described, natural aluminosilicate minerals, such as greensands and clays, or modification of these. In 1935 Adams and Holmes (*1*) prepared synthetic resins which were cation exchangers. If concentrated solutions of phenol (or, better, phenolsulfonic acid) (*2*) and formaldehyde are mixed, with an acid catalyst added if necessary, they will set to a brown or black gel. This can be dried to a porous mass which contains replaceable hydrogen ions. It has a chemical structure something like this:



The benzene rings are tied together in an endless insoluble framework, but the hydrogen ions of the sulfonic acid groups (and to a smaller extent, those of the phenolic hydroxyls) are free to be replaced by sodium ions or any other cations. The revolutionary importance of these organic cation exchangers is that the hydrogen ion can be exchanged just like any other cation. This is not possible in the aluminosilicates because acids will attack these porous materials very rapidly, liberating silica. The organic cation exchangers have certain other advantages, too. They are usually more rapid in their action, and some of them have a much higher capacity than the aluminosilicates; furthermore, they do not impart any trace of silicate to the water passing through them which is an advantage in treating water for high-pressure boilers (*3*, *13*).

A very useful organic-cation exchanger can be made from bituminous coal by treatment with fuming sulfuric acid or sulfur trioxide (*20*). Oxidation and sulfonation take place, and the product has sulfonic acid, carboxyl, and phenolic groups attached to a framework of fused benzene rings. These "sulfonated coals" do not have the capacity of the newer sulfonic acid resins, but they are cheaper and have better chemical stability.

The only successful commercial anion exchangers are organic in origin, being synthetic resins made by condensing polyamines with formaldehyde. These resins are insoluble bases of very high molecular weight; they will take up acids from solution as follows:

$$R_3N + HCl \rightarrow [R_3NH^{+}Cl^{-}]$$

or else

$$R_3NH^{+}OH^{-} + HCl \rightarrow [R_3NH^{+}Cl^{-} + H_2O]$$

The anion thus incorporated can be exchanged for other anions in the usual way.

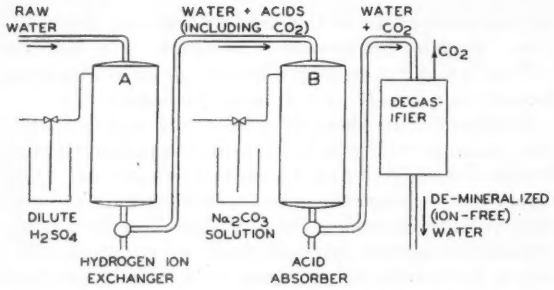


FIGURE 1. DE-MINERALIZATION OF WATER

The organic cation and anion exchangers have made possible the most significant advance in water conditioning in recent years—the complete removal of electrolytes from water without distillation (*22*). The principle used is shown diagrammatically in Figure 1. The water containing dissolved salts is first passed through a cation exchanger in tank *A* containing hydrogen ions; as it flows out of tank *A*, it contains no salts, but instead the corresponding acids. Then the water passes through an anion exchanger in tank *B*, which takes out the acid, leaving the water as free from electrolytes as if it had been distilled. (Carbonic acid is too weak to be entirely removed in tank *B*, but this is easily removed by aeration.) When the ion exchangers become exhausted, they are regenerated, the cation exchanger with dilute sulfuric acid, the anion exchanger with dilute sodium hydroxide or carbonate solution. The cost of purifying lake, river, or well water by this process is far less than by distillation, and many industries today are using this "de-mineralized" water which could not afford to use distilled water.

The ion exchange process will *not* remove dissolved impurities which are nonionized, such as sugar. It is, therefore, useful for removing dissolved salts from sugar juices; this is especially important in the beet sugar industry where the rather large electrolyte content of the untreated juice interferes with the crystallization of the sugar (*26*). By a similar process pure pectin can be obtained from citrus wastes.

Besides removing unwanted impurities, ion exchange can be used to recover valuable substances from solution. If a very dilute copper salt solution is passed through a cation exchanger bed, the copper ions are held back in the exchanger. They can be extracted with, for example, twice normal sulfuric acid to give a relatively concentrated copper solution from which crystals of copper sulfate can easily be obtained. The recovery of metals from electroplating wastes in this way has been proposed. Another possibility is to convert the metal into a complex anion and recover it with an anion exchanger; the recovery of chromate, vanadate, chloroplatinate, and other ions in this manner has been investigated (*19*). For such applications the organic exchangers are much preferable to the inorganic, as heavy metal ions, when absorbed by the latter, react with the aluminosilicate framework and will not come out again.

The use of ion exchange to recover metallic ions may or may not prove economical, but the recovery of organic ions has been very successful. Alkaloids, such as quinine or nicotine which form positive ions with the hydrogen ion, can be adsorbed very nicely on a hydrogen ion exchanger. They can be removed from the exchanger by regeneration with alkali together with a suitable solvent, such as alcohol or acetone (*18*). Vitamins can be recovered in this way; in the B complex, thiamin, which is strongly ionized, can be separated from riboflavin, which is weakly ionized and weakly absorbed (*9*). Tartaric acid can be recovered from grape wastes by using an acid-absorbing resin (*11*). One of the most interesting developments is in the separation of amino acids. These can be either anions or cations or else neutral, depending on the pH, and by using both cation and anion exchange, it is a fairly simple matter to separate, say, lysine, $H_2N{\cdot}(CH_2)_4{\cdot}CHNH_2{\cdot}COOH$, glycine, $H_2N{\cdot}CH_2{\cdot}COOH$, and aspartic acid, $HOOC{\cdot}CH_2{\cdot}CHNH_2{\cdot}COOH$ from one another. In approximately neutral solution (pH 6) the first forms cations, the third anions, and the second neutral molecules (actually "zwitterions," $H_3N^+{\cdot}CH_2{\cdot}COO^-$) (*4*, *5*). Pure amino acids produced in this way from protein hydrolyzates are used for intravenous feeding.

The separation of anions from cations has its use, too, in analytical chemistry. A notorious difficulty in quantitative analysis is the exact determination of sulfate in solutions which also contain iron or aluminum. Barium sulfate precipitated from such solutions is always contaminated with iron or aluminum, while if the trivalent metals are precipitated first as hydrous oxides, these hydrous oxides carry down sulfate with them. If the solution is passed through a hydrogen ion exchanger, the metal ions are retained by the exchanger, and the sulfate passed on as sulfuric acid, in which the sulfate ion is easily and accurately determined. The metals can be removed from the exchanger with hydrochloric acid and determined separately. Many other analytical separations are possible on these lines (*7*, *17*). In such work, sulfonated coals are far preferable to cation exchange resins because of their greater stability.

Ion exchange has applications in preparative chemistry. It is used in a beautifully simple method for making colloidal suspensions of hydrous oxides; sodium silicate solution, passed through a hydrogen ion exchanger, yields what would be silicic acid if there were such a thing, but is actually colloidal silica. Stable 20 per cent silica sols of high purity are made in this way by the tank-car lot and are used in the textile industry. Ammonium metavanadate solution gives colloidal vanadium pentoxide. Dilute ferric sulfate solution, passed through an alkali-regenerated anion exchanger, gives a red ferric oxide sol (*16*).

An application of ion exchange that has attracted much attention is the desalting of sea water. During the latter part of the war every United States Army and Navy plane which operated over the ocean carried as part of the equipment attached to the rubber life raft a small can containing a plastic bag and six tablets. Each

of these tablets kneaded in the bag with a pint of sea water would produce a pint of drinking water. The whole kit weighed less than a pound. The tablets were made of a special high-capacity ion exchanger, with silver as the exchangeable cation; the sodium and magnesium ions of the sea water were taken up by the exchanger while the chloride ions were precipitated as silver chloride. The conventional two-step de-mineralization process is unsuitable here as the available ion exchangers do not have a high enough capacity to cope with the high concentration of salts in sea water (*21*).

From these examples, the versatility of the ion exchange process is apparent. No longer is ion exchange confined to the one major application of softening hard water; it has a sufficiently general application that it deserves to rank with distillation, solvent extraction, and filtration as one of the unit processess of chemical industry.

LECTURE DEMONSTRATIONS IN ION EXCHANGE

1. Ion Exchange Made Visible: This experiment imitates the original experiments of Way, using colored ions and a modern high-capacity exchanger. A vertical tube of one of the forms shown in Figure 2 is closed with a plug of glass wool at the bottom and packed about half or two-thirds full with an organic cation exchanger of the "sulfonated coal" or synthetic resin type. This must be placed in the tube wet, as the dry materials swell a good deal when they take up water. The column is freed from air bubbles if necessary by "backwashing"—that is, by passing a stream of water upwards through the bed at a fast enough rate to loosen the granules. If the material is new stock it is a good idea to rinse it with concentrated hydrochloric acid followed by plenty of water. The bed should not be allowed to drain, or it will have to be backwashed again; it should be kept covered with water.

The exchanger is now saturated with the cobalt ion by passing a five or ten per cent solution of cobalt sulfate or nitrate until the solution coming out of the bottom is as pink as that going in at the top. The bed is then washed out with distilled water. All the above should be done before the lecture.

It can now be demonstrated that washing the exchanger with distilled water does not dissolve out any cobalt. But when a dilute nickel chloride solution (10 grams of $NiCl_2 \cdot 6H_2O$ per liter) is passed, the pink cobalt solution will be seen flowing out the bottom of the exchanger bed while the green nickel solution flows in at the top.

2. Preparation of an Ion Exchanger: Solutions of sodium aluminate (0.5 *M* in aluminum) and sodium silicate (ordinary water glass diluted with twice its volume of water, 1.0 *M* in Na^+, 3.2 *M* in SiO_2) are prepared beforehand. Fifty milliliters of sodium silicate solution are poured into a 400-ml. beaker and swirled around while 100 ml. of sodium aluminate solution are poured in. The mixture sets in two or three seconds to an opalescent gel, and the beaker can be turned upside down without anything falling out.

This demonstration goes over well and emphasizes the extreme porosity of the aluminosilicate exchangers; the gel, although quite stiff, is mostly water.

3. Water Softening: An exchanger tube of the type shown in Figure 2, but much wider, is used. It should be about 5 or 6 cm. wide, with the exchanger bed about 15 cm. deep. Any good cation exchanger will do; the writer uses the aluminosilicate, "Decalso," in a fine mesh size (about 40–80 mesh). Carbonaceous exchangers work faster and do not need to be of fine mesh. The bed is treated with saturated sodium chloride brine and washed well with water before starting.

To test the hardness of the water, a soap solution is necessary. The writer uses a *M*/25 solution of potassium palmitate in a 1:1 *n*-propanol-water mixture ("Blacher's solution"), colored with a little methylene blue. This is placed in a buret backed by a white card with legible graduations.

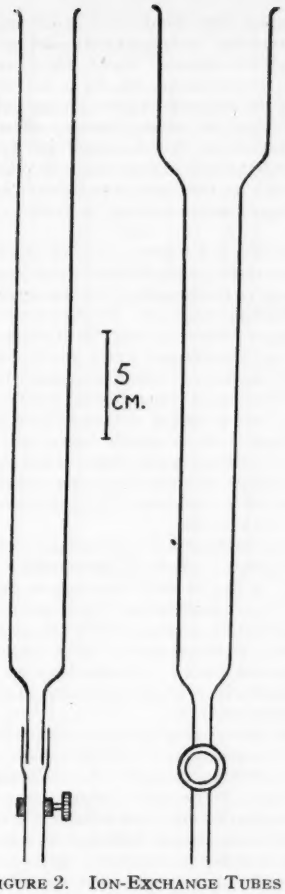


FIGURE 2. ION-EXCHANGE TUBES

For the demonstration, tap water is run through the exchanger bed at about 100 ml. per minute. The first 100 ml. of effluent, which includes the liquid that was in the bed at the start, is discarded; the next 200 ml. is collected in a 500-ml. graduated cylinder. While this is flowing, a second cylinder is filled to the 200-ml. mark with tap water, and soap solution is added to it from the buret, a little at a time. After each addition, the water is shaken vigorously, placing the palm of the hand over the end of the cylinder while so doing. Nothing happens for a while except the production of a curdy precipitate. Comments from the lecturer on the waste of soap in our hard-water cities are in order. When finally a lather is formed, the volume of soap is noted and the cylinder set out on the lecture table. The cylinder of softened water is then taken, one ml. of soap solution is introduced, and the cylinder shaken. A stable lather forms immediately. The cylinder is set beside the other one. The untreated tap water is very turbid in contrast to the almost clear soft water, and the much darker blue of the former testifies to the greater soap consumption. The soft water lather will probably last longer, too.

Lake Michigan water, of hardness 2.5 meq./liter (125 parts per million, or 7 grains per gallon, as $CaCO_3$), takes about 15 ml. of *N*/25 palmitate solution to give a lather. The consumption of other waters can be gaged accordingly. In testing the soft water, the lecturer should see that he does not have chalk dust on the hand he uses to close the cylinder while shaking, for obvious reasons.

4. De-Mineralization of Water: The writer uses an apparatus like that described by Nachod and Sussman in THIS JOURNAL,

21, 56 (1944) except that the dropper at the top of the acid removing tube is omitted. A one per cent solution of $CuSO_4 \cdot 5H_2O$ is passed through the columns. Some effluent is taken from the bottom of the cation-exchanger column as well as from the outlet at the bottom of the anion-exchanger column, and both are tested with methyl orange, the cation-exchanger effluent testing acid. They are also tested for electrical conductivity with a pair of electrodes and a light bulb. Some more de-mineralized effluent is then collected. At this point the lecturer feels thirsty and shows the courage of his convictions by drinking the de-mineralized water.

After regeneration and before re-use, the acid absorber needs a good deal more rinsing with distilled water than the cation exchanger; it is apt to retain some of the regenerant, particularly if sodium hydroxide has been used. The writer once lent his apparatus to a colleague without having rinsed this bed properly; the lecturer drank the first effluent which was free from copper sulfate, to be sure, but was not free from sodium hydroxide. Stoically the lecturer refrained from comment until afterwards.

After about a liter of copper sulfate solution has been passed, the cation-exchanger column can be regenerated on the lecture table with 1–2 *N* sulfuric acid. A quite concentrated, strongly colored copper sulfate solution comes out of the bottom, which provides the cue for a discussion of metal recovery, alkaloid recovery, etc., by ion exchange.

5. Colloids by Ion Exchange: [Reference: RYZNAR, *Ind. Eng. Chem.*, **36**, 821 (1944).] Hydrous ferric oxide sol makes a good demonstration. A bed of acid-absorbing or "anion exchange" resin, about 2 cm. in diameter and 15–20 cm. in depth, is used. If it is new material, it is treated with excess 2 *N* hydrochloric acid and washed. It is regenerated with ammonia water, then washed with at least 250 ml. of distilled water. Just before the lecture, it is rinsed with a little more water and about 50 ml. of *N*/100 hydrochloric acid.

A solution of 2 grams of anhydrous ferric sulfate and 1 ml. of 6 *N* hydrochloric acid in a liter of distilled water is suitable. This is passed at 50 to 100 ml. a minute. A clear orange red sol flows out at the bottom. To be certain of obtaining a clear sol, it is essential to have chloride ion in the influent; ferric sulfate solution with sulfuric acid added to check hydrolysis is very liable to give a turbid effluent or to deposit ferric oxide in the bed. A solution of ferric chloride with added hydrochloric or sulfuric acid can be used, but this is distinctly yellower than the solution described, and the paler the color of the influent, the better the demonstration.

The ferric oxide sol can be shown not to conduct electricity. It is a positive sol and can be used to demonstrate the relative efficiency of chloride and sulfate ions in coagulation. For this purpose a fresh sol is better than one which has been standing a day or two.

Vanadium pentoxide sol, which can be made very easily from saturated ammonium metavanadate solution and acid-regenerated sulfonated coal cation exchanger, is suitable for demonstrating streaming birefringence. The sol is first heated for an hour on the steam bath, when the particles get larger and the color changes from yellow to a rich brown. It is then filtered if necessary, and some of it is put in a beaker on the stage of the kind of lantern slide projector in which the slide is laid horizontally above the condensing lens. Underneath the beaker and on top of it are crossed Polaroid plates. While the sol is at rest, little or no light passes through, but when the contents of the beaker are swirled around, the "cross of isocline" is seen projected on the screen.

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EDITOR'S OUTLOOK (*Continued from page 417*)

sociation." H_2O doesn't describe all the molecules, nor H_4O_2, nor H_6O_3. Hydrogen atoms can play a sort of "pussy-wants-a-corner" game among the oxygen atoms, or at any rate some of them can. So we never know just where, nor what, our atomic grouping is.

In many liquids, and in many typical solids, the atomic grouping into molecules is perfectly definite and practically permanent; their formulas indicate not only the composition but also something of the molecular structure. Unfortunately, there is nothing which identifies such formulas. Furthermore, there are many substances which do not fall completely into the category of "molecular substance" on the one hand, or "nonmolecular" ("ionic") on the other. In fact, it is probably better to say that every substance is somewhere between the two extremes.

In other words, it is time we gave up some of our fairy stories about molecules. It should not be difficult to give, early in our courses, a brief summary of some of the things we *know* about molecular structure, and to emphasize that until we know how atoms are actually arranged in a given case, it is useless to worry about the nature of the forces between them or what holds them together.

Low-Ester Pectins In Ready-To Serve Salads

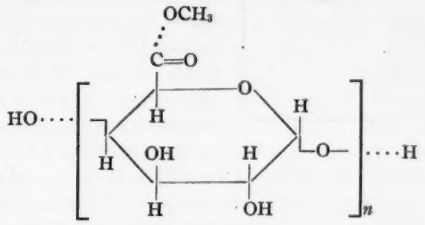
Fruit spreads depend upon pectin, sugar, and acid in proper proportions to form a jelly. With ordinary pectin, jelly will not form at much below 65 per cent soluble solids, the legally defined lower limit. Pectin gel (jel) formation was once thought to be due to "dehydration" or removal of moisture from pectin solutions by such substances as sugar, glycerin, and alcohol. A better explanation is that gel formation or gelation is caused by hydrogen-bonding, as all these gel-forming substances are hydroxyl derivatives and good hydrogen-bonding agents.

Recent developments in pectin chemistry make possible the preparation of pectin gels by ionic bonding. For example, calcium reacts with specially prepared pectin to give a calcium salt in the form of a gel. The calcium in fruit juices is almost sufficient for this purpose; sugar can be used in any amount desired for flavoring and is not necessary for gel formation. This discovery presents the opportunity for developing a series of ready-to-serve fruit and vegetable salads, aspics, and fruit desserts. The fruit juice in ordinary canned or frozen fruits for salad can be jelled with the proper amount of low-ester pectin to form very attractive salads or desserts. Upwards of 20 million units of this product were packed for Army use in cans for individual servings and met enthusiastic reception on fronts where fruits and salads were rare sights. Also tomato juice can be spiced and gelled with low-ester pectin to form tomato aspic. To serve a delightful salad the housewife cuts the top and bottom from the can, slides out the gel, slices it onto a leaf of lettuce, and adds her favorite dressing.

The development of low-ester pectin has helped to elucidate the structure of pectin. Most properties of pectin can be explained on the basis that it is a linear high molecular-weight polymer of galacturonic acid, partially esterified with methyl groups. Many factors, such as degree of esterification and galacturonide and ash content of preparations as commonly obtained, greatly influence the behavior. A true picture cannot ignore the possible influences exerted by impurities. Confusion often arose by trying to determine the structure of pectin on the basis of properties caused by impurities or by congeners, such as araban and galactan.

We may write a working formula for pectin as shown in the diagram where n may denote as many as a thousand galacturonide units in a pectin of molecular weight of 200,000.

Not all the carboxyl groups are esterified. In fact, 70 to 75 per cent esterification appears to be the maximum in natural apple and citrus pectin. Where ester groups are removed the acidic



properties increase, and if completely removed, insoluble pectic acid results. If only partly removed (20 to 50 per cent esterification) the product remains soluble but is reactive with metallic ions.

There are three methods by which low-ester pectins can be prepared—namely, acid hydrolysis, alkaline saponification, and enzyme hydrolysis using pectase. Acid hydrolysis depolymerizes the pectin molecule to some extent, but careful selection of time, temperature, and pH for hydrolysis permits the preparation of low-ester pectins in the useful range of esterification (30 to 40 per cent) while still retaining high molecular weight. Similarly, alkalies lower the molecular weight. Strong alkalies cannot be used, but with ammonia at lowered temperatures useful products are obtained. Many pectase preparations contain more or less pectinase, an enzyme that depolymerizes pectin; but by selection of pH values favorable for pectase activity and unfavorable for pectinase action, preparations can be obtained with practically no degradation. All three methods will shortly be in use for commercial preparations of this new pectin and accordingly we may expect to see new food products in which they are employed appear in the market at any time.—Reprinted from the *Nutritional Observatory* (May, 1946).

RUBIES AND SAPPHIRES (*Continued from page 422*)

produces relatively round spots while synthetic ruby yields dumbbell-shaped spots, the latter not always too clearly defined. The reason may be that synthetic corundum is always badly strained. However, a great deal of work remains to be done in this field before a satisfactory interpretation can be made.

The question is frequently asked, "Will synthetic corundum supplant the demand for the genuine gem?" The answer is no. The connoisseur and patron of fine things will always buy sterling silver instead of plated and genuine oriental pearls in lieu of the Japanese cultured variety. And America, being what it is, the man who can only afford costume jewelry today may well be the one who will buy genuine rubies and sapphires tomorrow!

The writer is indebted to Tiffany & Company, Inc., to Mr. B. W. Anderson, director of the London Chamber of Commerce Gem-testing Laboratory, and to Mr. A. K. Seemann of the Linde Air Products Company, for kindly supplying the photographs and photomicrographs for this article.

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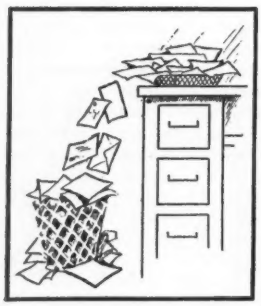

Out of the Editor's Basket

DANGER of explosions in plants producing oxygen by the liquefaction and rectification of air may be reduced by eliminating acetylene and other hydrocarbons from the air. Evidence of the explosive effect of acetylene and other hydrocarbons upon oxygen under production is scanty, according to a published report; however, the coexistence of solid acetylene and liquid oxygen at some point in operating units where explosions have occurred seems to indicate that this combination is a danger factor. Acetylene, the most important impurity, may be removed by both catalytic oxidation and adsorption on active charcoal.

Among the contaminants mentioned as being found in small quantities in ordinary air, particularly in industrial areas, are ozone, nitrogen oxides, carbon monoxide, acetylene, and other hydrocarbons. The danger attending the accumulation of ozone in oxygen units has been emphasized.

Spinel

A process for hardening synthetic spinel jewel bearings to the point where their performance approached that of synthetic sapphire bearings was developed by the Germans during the war, according to a recent report.

Spinel, a crystalline mineral, is normally considered less satisfactory for bearings than sapphire because it is softer. For the same reason it is easier to work and requires less diamond powder for cutting. This was an important consideration in Germany because of the severe diamond powder shortage.

The German hardening process involved heating the spinel to a temperature of 950 to 1050°C. for 12 hours. This precipitated the excess alumina in the spinel and converted it to a different alumina form. As a result the clear spinel turned cloudy and became harder. Final polishing of the bearing surface after heat treatment was done with diamond powder in the usual manner.

According to the German inventor of the process, spinel bearings would have been produced on a much wider scale in Germany had it not been for the opposition of the I. G. Farbenindustrie which made sapphires.

Penicillin for Teeth

And now comes penicillin tooth powder! It seems it is based upon investigation carried out by Dr. T. J. Hill of the Western Reserve University who found that when penicillin was used daily in the tooth powder of a large number of school boys, the oral bacterial count dropped from an average of 72,000 to 300 in three weeks. On discontinuance, the count went up again.

Gold-Germanium Alloy

We credit *Aminco Laboratory News* with this item:

A gold alloy with low-melting and other unusual properties was described recently by Dr. Robert I. Jaffee of the Battelle Memorial Institute, Columbus, Ohio, where the alloy has been studied.

It is a gold-germanium alloy, 88 per cent gold and 12 per cent germanium, that melts at 673°F., only 50 degrees higher than the melting point of lead. It is what scientists call a gold-germanium "eutectic," a term applied to an alloy with a lower fusing point than its components have by themselves. Gold melts at 1945°F., and germanium at approximately 1760°F.

This "eutectic" is harder than ordinary gold and has superior wearing qualities. Another property of the alloy is its slight expansion on solidification which compensates for contraction in cooling to room temperature. Because of this property, extremely precise castings, such as dental inlays, can be made, and these dental castings would require no correction to take care of shrinkage that occurs with most alloys.

Because of the low melting point of the alloy, it can be used as a solder by jewelers. Gold-coated jewelry of long-wearing properties can be made by merely dipping the object to be plated into the molten eutectic.

The chief interest in the metal at present, Dr. Jaffee stated, is its potentialities as a rectifier in radar equipment.

Fused Quartz

A new German process for making fused quartz of precision optical quality was recently revealed. The fused quartz was used in making one-piece optical squares, which were an essential part of the Type R40 four-meter Zeiss range finder. It was made from standard Brazilian crystals, but instead of using the usual vacuum furnace process, special techniques of building up quartz rods and of welding these rods into integral blocks were developed. From these blocks blanks of excellent optical quality could be cut.

Synthetic Mica

Synthetic, crystalline fluorine-mica was developed on a laboratory scale by the Germans during the war in an effort to offset the shortage of natural mica, according to reports. The synthetic product corresponded to natural muscovite ("Phlogopite") mica, widely used in the electronic industries.

During crystallization, two forces are directed perpendicularly to each other—(1) a directed gradient of temperature (vertical direction) and (2) a magnetic field (horizontal direction). Owing to the paramagnetic qualities of the compound, the crystals are oriented in the plane of the magnetic field. This affects the horizontal growth of the mica and gives rise to the laminations characteristic of natural mica.

A carbon crucible, capable of withstanding temperatures higher than 1300°C., was used for production of the synthetic mica. Cooling of the melts was as slow as possible because of the narrow interval between melting and crystallization temperatures. The systematic synthesis of mica was made possible by earlier X-ray studies of its structure and by application of the fundamental laws of crystallography and chemistry.

Beryllium

Germany and Italy succeeded in producing only 20.6 tons of beryllium during the war, according to a report by B. B. Sawyer, President of the Brush Beryllium Company, Cleveland, Ohio, and H. A. Sloman of the National Physical Laboratory, Teddington, England.

The investigators found the Axis beryllium industry considerably less developed than that of the United States. In Germany, the three phases of the industry—extraction, heavy alloys, light alloys—were allocated to separate firms. The Deutsche Gold und Silber Scheide Anstalt produced beryllium oxide, chloride, metal flakes, and a small amount of 20 per cent beryllium-aluminum master alloy. Heraeus Vacuumschmelzer consumed these products in making heavy alloys. I. G. Farbenindustrie, in making light alloys, also consumed beryllium chloride and aluminum alloy but derived most of its supply of the latter from an Italian firm. The Italians made no pure beryllium metal.

The German beryllium industry during the war was concerned primarily with heavy alloys and with a 0.2 per cent aluminum alloy, used for sand cast cylinder heads of airplane motors. One firm sold technical beryllium oxide for the production of beryllium-copper alloy, refractory ware, and dental cements. Pure beryllium oxide was used chiefly in the light metal industry. Beryllium metal was sold mainly in the form of electrolytic flake. Beryllium-copper alloys were produced and sold as forgings, stampings, rolled plate, and drawn rod and wire. Small quantities of beryllium carbonate, nitrate, and sulfate were produced.

Shark Repellent

An effective shark repellent, consisting of copper acetate and black water-soluble dyestuff bonded with a wax binder, was developed by the Navy during the war. Field tests conducted in shark-infested waters, using bonita, mullet, and bloody fish as bait, revealed that copper acetate, diffused slowly into the water, repelled sharks; however, since sharks have both an olfactory and a visual response to food, a black dyestuff was added to make it more effective. The composition of the mixture was about 20 per cent copper acetate and 80 per cent black dyestuff.

For individual use by persons adrift in shark-infested water, the repellent was packed in a bag similar to a large tea bag and attached to life jackets. When allowed to hang loose in the water, the repellent slowly diffused and set up a large dark-colored area around the user. One unit or bag gave protection for about three hours. Users were cautioned to hang the bag below the water to give protection to the lower parts of the body.

Tomato Antibiotic

A new antibiotic substance is reported to have been derived from the tomato plant. This substance, called "tomatin," attacks especially the fungi that produce ringworm and athlete's foot.

"Foampreservers"

A protective "foam suit" which enabled men who fell into the sea to keep warm for two to three hours was developed in Germany during the war, according to report. A foam-producing powder was rubbed into the wool-like pile of the acetate rayon middle layer of the three-layer garment. The powder generated foam immediately upon contact with sea water. Foaming continued for a long period, even when the powder was greatly diluted. The resulting layer of foam between the middle and outer fabric layers of the suit protected the wearer from an excessive drop in body temperature.

Foam powder for use in the North Atlantic and the North Sea contained sodium bicarbonate, citric acid crystals, benzoic acid crystals, a gelatin emulsion, and two other chemicals bearing the German trade names "Igepon T" and "Gardinol B."

Carbon Monoxide

The Germans developed an apparatus for the instantaneous testing of air for carbon monoxide. It utilizes self-sealing tubes of silica gel through which air is pumped. One layer of the gel is impregnated with concentrated sulfuric acid. The other layer, impregnated with oleum and iodine pentoxide, changes to greenish violet in the presence of carbon monoxide. The tester is a compact unit, having nine detector tubes and a metal pump with which the sample of air is brought into contact with the test gel.

New Journal

The *Journal of General Education* will make its first appearance in October, published by the State University of Iowa. Its field is announced to include some of the informal branches of education, recognizing that these are as important as the school and formal classroom.

Corrosion Protection

A new illustrated booklet dealing with the use of magnesium anodes for cathodic protection has just been published by the Magnesium Division of the Dow Chemical Company, Midland, Michigan. Descriptive information regarding this method of corrosion control is presented along with answers to some of the more commonly asked questions concerning this subject.

Fireproofing Paint

American wartime research on paints revealed that the addition of aluminum powder to priming coats improved the fire-retardant properties of paint used on the interior surfaces of Navy ships.

In the past the Navy had reduced fire hazards caused by paint coatings by removing all old paint from interior surfaces and refinishing with not more than three coats of new paint. Paint formulas had also been revised to reduce inflammability; however, much better results were obtained by adding 80 per cent aluminum paste to the primer in the proportion of one pound of paste to two pounds of primer.

Heavy Carbon

We credit *Aminco Laboratory News* with this item:

Carbon of atomic weight 13, for use in research on cancer, diabetes, arterial, heart, and other diseases, will be produced in substantial quantities, according to a recent announcement of the Sun Oil Company and the Houdry Process Corporation. The anticipated production of this heavy carbon isotope is expected to increase from 500 to 1000 times the world supply of this chemical element.

The cost is expected to be brought down to about $40 a gram. The experiments were started with less than a half-gram which cost several thousand dollars to concentrate.

Carbon 13 serves as a tracer in chemical reactions in living and nonliving material, since by its different weight it can be spotted and told from ordinary carbon.

The work was carried on by Dr. Aristid V. Grosse and Dr. A. E. Smith of the Houdry organization, Dr. Stanley P. Reimann of the Lankenau Hospital Research Institute of Philadelphia, and others of these two organizations.

Night Vision

The Japanese claim that a proprietary drug called "Migozai" improved night vision of soldiers 150 to 200 per cent, according to a U. S. Army Air Forces report. The drug was administered as a yellow-colored pill, one centimeter in diameter. The pill contained 5000 international units of vitamin A in the form of cod-liver oil, crucuron powder as a cholegogue, lecithin as a stabilizer, calcium phosphate, and sugar. A dosage of three tablets three times a day for two days was said to create a blood level of vitamin A which lasted about three days. The drug was readministered on the fifth and sixth days.

Cerium

It is said that the Germans had made considerable progress in the use of cerium before their supplies were exhausted during the war. According to investigators, German engineers achieved 20 per cent higher extraction of the metal from monazite sand than is possible with methods now known in the United States. They have also developed techniques for working cerium in powder form.

The chief uses of cerium are (1) to produce steel alloys and aluminum and magnesium alloy castings for jet-plane gas turbines, aircraft supercharger parts, and other equipment demanding great tensile strength at high temperature, (2) to produce a vacuum in electronic tubes by absorbing the oxygen remaining in the glass when it is sealed, and (3) as an igniter in torches for acetylene welding, in cigarette lighter flints, and in miners' head lamps.

Safety Hint

The following comes from the Safety Research Institute: Prevention of exposure to organic solvents or their vapors is the objective of every solvent safety program. Yet accidents can and do occur. However, prompt first aid followed by proper medical treatment will generally avoid injury. Following are first aid measures for exposure to organic solvents:

If an individual is affected by the inhalation of solvent vapors, so that he develops dizziness, nausea, headache, irritation of the eyes or respiratory tract, or other signs of illness, he should be immediately removed to a solvent-free atmosphere. If unconscious, he should be placed on his back and covered to prevent chill. If breathing has stopped, prone pressure artificial respiration should be given. *Under no circumstances should alcoholic stimulants be given to individuals exposed to solvents. Serious injury may result.*

If solvent is swallowed, the individual should be made to vomit immediately.

If solvent enters the eyes, they should be washed promptly with large amounts of water for at least 15 minutes. For this purpose it is advisable to use a low-pressure supply of water at room temperature in order to avoid shock.

If a large quantity of solvent spills on the skin, it should be washed off and an emollient cream applied.

If solvent spills on clothing (except where safety or solvent-resistant clothing is worn), wet clothes should be removed, the body washed, and an emollient cream applied where the solvent has penetrated. Clothing should be dried outdoors or where evaporating vapors will not be inhaled and should not be worn again until free of solvent odor.

Following first aid, prompt medical attention should be obtained. This is of special urgency where solvents have been taken internally or where an individual feels acutely ill from the inhalation of vapors. Serious injury may result where such cases are neglected, whereas prompt medical treatment usually brings complete recovery.

Dental Hygiene

Tablets containing fluorine compounds, to be melted in the mouth in order to ward off dental decay, will be available soon on prescription. Chewing gum containing vitamin K is also said to be a good preventive. Meanwhile, experiments with an alloy containing germanium promise good results in dental inlays.

Wartime Chemical Education Through E.S.M.W.T.[1]

AUSTIN M. PATTERSON

Antioch College, Yellow Springs, Ohio

IN 1940 our industries were feeling the stimulus of the war in Europe and it seemed probable that the United States would eventually be drawn in. Many workers were employed on jobs requiring new skills and hence new training. It soon became evident that the normal sources of training, both within industry and outside, were not sufficient to meet the situation and that the Government must help. Accordingly, late in 1940 legislation was enacted by Congress providing for courses in vocational education below the college level and also for courses of college grade and beyond. Both programs were under the direction of the U. S. Office of Education and both were maintained during the remainder of the war, but we are concerned here with the higher program only.

The college-level program as originally framed was designed to meet the shortage of engineers in fields essential to the national defense. It was named Engineering Defense Training and commonly referred to as E.D.T. The term "engineer" was interpreted rather liberally to mean anyone engaged, or about to be engaged, in work of an engineering nature, and all recognized branches of engineering were included in so far as they could contribute to the national defense. Courses of this nature continued to be the largest part of the program to the end of the war; however, the need for extending the training to chemists, physicists, and production supervisors soon became evident and was met in 1941 by a new act. Under this act the program was continued with the title Engineering, Science, and Management Defense Training, or, by initials, E.S.M.D.T. By 1942 the United States was in the war and the title was again changed by substituting the word "War" for the word "Defense," thus making it Engineering, Science, and Management War Training, or E.S.M.W.T.

The plan of the work was this. An agency was set up within the U. S. Office of Education to direct the program. The nonprofit degree-granting institutions of the country were invited to apply for admission to the program in all cases where a need was observed for training which they might meet through the program. Only those schools were approved which were of good repute and which during the past year had granted degrees to majors with adequate training (at least 18 semester hours of junior and senior work in the major, or its equivalent) in one or more of the four fields covered by the program. Practically all the leading institutions having majors in these lines did participate. Courses were given under the program by 227 universities, colleges, and technical schools.

Each institution appointed a representative who conducted the dealings with the Washington office. It was his duty to ascertain the training need in his locality by conferring with employers and foremen, by advertising, and in other ways. He then submitted for each proposed course a preliminary proposal, stating the purpose of the course, an outline of its content, the names of the prospective teachers with their rates of payment, apparatus or other supplies needed, and an itemized estimate of the cost. Approval of this proposal carried with it authorization to start the course. After the course got under way and the number of trainees became known, the representative submitted a final proposal which included a budget based on actual operation. As soon as the final proposal was approved, federal funds for the entire course were made available to the institution whose financial officer then administered them as a trustee of the Government. No tuition was charged, but the trainees were expected to buy textbooks and such other supplies as students ordinarily furnish. When the course was conducted on the property of the school, this was furnished rent-free (though heat, light, etc., could be charged for), and in return the institution received title to the equipment furnished by the Government for use in the course. Much of the equipment was used over and over again in succeeding courses. It ranged from test tubes to costly apparatus like mass spectrographs, depending on the need for it and on a percentage limitation. The institutional representative was required to make monthly reports of the monies expended and a final report at the end of each fiscal year.

The last E.S.M.W.T. courses were started on or before May 15, 1945, and all were terminated by June 30 of that year. During the life of the program 42,568 courses were given in which total enrollments numbered 1,795,716 (individual trainees numbered slightly over 1,500,000, some of whom were enrolled in more than one course). The enrollments in courses for chemical engineers were 52,020, for chemists 38,838, and for training engineers in basic chemistry 4275.

There was great variety in the content of the courses. In the chemical field, besides the usual courses in analysis and in general, inorganic, organic, and physical chemistry, may be mentioned glass blowing, laboratory techniques, biochemistry, chemical thermodynamics, colloidal and surface chemistry, industrial preparations, photographic chemistry, pharmaceutical chemistry, and the chemistry of several applied fields, of

[1] Presented, in substance, before the Dayton Section of the American Chemical Society, February 9, 1946.

which the most prominent were explosives, petroleum, metallurgy (not included in the above enrollment figures for chemical engineering or chemistry), rubber, plastics, and paint and varnish.

The law required that these courses be short. They rarely extended beyond 18 weeks and were often given for only 16 or 12 weeks or even less. Most of them were in-service courses, given in the evening (usually two or three evenings a week) to persons employed in the daytime. Some, however, were intensive full-time courses lasting four to six weeks for persons preparing to take a new job. Such a course was given, for example, by the University of Pittsburgh to previously untrained women who were wanted as operators in a synthetic rubber plant. There was good psychology in the short course in that the trainees were more likely to finish and to have a sense of definite accomplishment. Each E.S.M.W.T. course was designed to prepare for some definite war job; if the trainee then wished to take another course to prepare himself for promotion to a better job, there was no objection to such a procedure, and sequences of courses were in fact planned to accomplish this purpose.

Attendance in the courses averaged about 42. Some of the classes were considerably smaller; on the other hand, one course might have a number of sections in different places. Pennsylvania State College, for example, already had a state-wide extension system and used its instructors in giving E.S.M.W.T. courses in many sections in many parts of the state. As may be imagined, many of the courses were of freshman or sophomore level, but a considerable proportion were higher. To give only two instances, some of the radar courses were open only to those of high previous training, and in advanced courses in inorganic, organic, and physical chemistry given by Professor H. S. Taylor and members of his Princeton staff, most of the trainees were Ph.D's. These latter courses were given to chemists in the crowded New Jersey industrial area near New York, and Dr. Taylor and his colleagues often had to stay overnight after their classes. Rutgers also gave many courses to competent chemists in this area.

Now let us consider the Washington organization. Since the training program was inspired by engineers and since engineering courses were always the principal part of it, one need not wonder that an engineering atmosphere prevailed. Dean A. A. Potter of Purdue University had a large part in establishing the program, and to its close he served as Chairman of the National Advisory Committee and as consultant to the Office of Education. The first director, Dean Roy A. Seaton of Kansas State College, was a very competent and meticulous administrator. When he returned to his institution in 1942, Dean George W. Case of the University of New Hampshire became his worthy successor. Consulting with the Director was a National Advisory Committee which included a number of the top technical teachers of the country. Naturally most of them were engineers, but chemistry was represented by Professor Norris W. Rakestraw of Brown University and physics by Dean Homer L. Dodge of the University of Oklahoma. It was my privilege to attend some of the meetings of this committee, and they always proved lively.

For E.S.M.W.T. administration the country was divided into 21 regions which fitted in with, but were not exactly the same as, the regions of the War Manpower Commission. Each region had a Regional Adviser who helped to keep things running smoothly among the institutions and who also met with the other regional advisers from time to time.

Our office staff at its peak comprised about 80 full-time employees, of whom about 30 had professional degrees. Several of these passed upon engineering proposals; there was one specialist each for chemistry, physics, and management courses, and there were field representatives, auditors, and statisticians. Each proposal and report was carefully examined, unit costs were computed, and correspondence or telephone conversation was often conducted with the institutional representatives and regional advisers. The atmosphere was one of earnest work such as might be expected to characterize a war agency. The members worked well and happily together, and we took pride in belonging to a staff that was businesslike, efficient, and absolutely straightforward and honest.

Our relations with the institutions were almost uniformly pleasant. Occasionally there would be fear that a desire to get new equipment or to secure work for faculty members might be too strong a motive in proposing some course, and such cases were investigated with care; but in general the schools gave loyal patriotic service and we know that many made sacrifices to do so. The intention of Congress was that the institutions should have neither financial profit nor loss from the program; but if they have derived benefit from the equipment which they are entitled to keep or were assisted in tiding over a period of reduced enrollment, we should be glad. After all, these are nonprofit institutions performing a great service to the nation, and the attitude of our Government toward them is generous.

That brings me to questions of cost. The total amount spent for the entire program was in round figures $60,000,000. This corresponds to an average of about $33 for each trainee for each course. What return did we as taxpayers get for that sum? The program was, of course, an emergency measure. Employers were swamped with new demands which involved the training of workmen and with a great turnover of workers as the draft became effective. There seems no question that E.S.M.W.T. helped materially to win the war; hundreds of letters from management were evidence of this. Of course the credit goes to the institutions; the Washington office was only the clearing house. This result alone would justify the expenditure.

But I believe there have been other benefits which carry over beyond the war. First, increased efficiency of large numbers of workers for peacetime industry. Second, increased appreciation of the value of such courses on the part of both management and labor;

many of the institutions, or in some cases their teachers, are continuing to give instruction of the E.S.M.W.T. type on a fee basis. And third, the influence which E.S.M.W.T. experience may have on the regular professional curricula. Teachers of these short emergency courses were forced to eliminate dead material and get down to a direct practical approach, "to brass tacks," not to eliminate theory necessarily, for some of these courses were all theory, but to discard material unnecessary for the purpose at hand. If these benefits prove themselves, we can regard E.S.M.W.T. as not only a war measure but a permanent investment in the future.

The cordial relations established between the Government and the engineering colleges are being maintained through a liaison officer, Mr. Henry H. Armsby, formerly Field Coordinator of E.S.M.W.T. and now Specialist in Higher Education in the U. S. Office of Education. I am indebted to Mr. Armsby for the final figures on E.S.M.W.T. and for criticism of this paper.

Laboratory Acid Cleaning Bath

GILBERT E. MOOS

Celanese Corporation of America, Newark, New Jersey

LABORATORIES which are not large enough to warrant the purchase of a large and expensive stoneware acid cleaning bath will probably find the following unit helpful in cleaning glassware, especially if engaged in research on resinous materials. Alkaline cleaning baths have been proposed[1] because of the danger involved in heating chromic acid cleaning solutions; however, hot chromic acid cleaning solutions are still preferred cleaning media, especially for sticky resinous residues which are frequently highly resistant to alkaline cleaning solutions. The apparatus described below was evolved from the need for thoroughly cleaning many thick-glass narrow-mouth bottles, multi-way stopcocks, still-heads, plate-glass, and other odd-shaped glass apparatus contaminated with resinous materials which were refractory to alkaline cleaning solutions and rinses of acid cleaning solutions.

A discarded iron stool was sawed off to a height of $8^1/_2$ inches and placed on a piece of transite board in turn placed on a piece of 1-inch asbestos resting on a standard soapstone laboratory bench. Two layers of asbestos board were placed on the seat of the stool, and an enameled $5^1/_2$-gallon pot was placed on the asbestos board. Two more layers of the asbestos board were placed inside the pot, and a $4^1/_2$-gallon Pyrex jar (12″ × 12″) was placed on the asbestos in the pot. A standard dichromate cleaning solution was prepared[2] using technical sulfuric acid. A piece of plate glass was placed on top of the Pyrex jar to limit most of the vapors of the hot solution to the container, leaving a small space between the glass plate and the inside edge of the jar to prevent any pressure buildup during heating. Two Bunsen burners and a Meker burner have been used to heat the bath. One-inch asbestos board has been placed around three sides of the stool to localize the heat of the burners.

The glass apparatus to be cleaned may be immersed in the acid by means of a long pair of forceps, but preferably it is suspended by pieces of Nichrome wire, which has a remarkable resistance to the acid cleaning solution. After immersion for a length of time (*e. g.*, 1 to 60 minutes) dependent upon the temperature of the bath as well as the nature and the amount of the resinous residue, the apparatus is removed from the bath with the aid of a pair of forceps when necessary and placed in an enameled tray—adjacent to the bath—to cool before being rinsed off with tap and distilled water. (In certain cases the glassware is rinsed with dilute alkali to remove residual acid which is claimed to have a strong affinity for glass.[3])

This unit has worked satisfactorily for about a year, the only maintenance being additions of 25 to 50 grams of chromic anhydride infrequently and about a liter of concentrated sulfuric acid once. If the Pyrex jar should break, the enameled pot will safely hold the cleaning solution until it can be removed. The Pyrex jar is considered to be better than an enameled pot as the immediate container for the acid because enameled ware is prone to cracking, chipping, and even chemical attack by some acids which may be formed in the acid cleaning solution. As a temporary safety container, however, an enameled pot is satisfactory even if slightly chipped or cracked.

As a substitute for the iron stool, a large standard tripod (*e. g.*, multiple ring variety) would probably serve satisfactorily; or a large electric heater or heaters can be used in place of the stool and gas burners,[4] as is being done in another laboratory of this department. Five- or six-gallon enameled pots can be purchased at a cost of four to five dollars, the Pyrex jar for six dollars.

[1] GADDIS, S., J. CHEM. EDUC., **19**, 368 (1942).

[2] KOLTHOFF, I. M., AND E. B. SANDELL, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, **1936**, p. 222.

[3] WAISBROT, S. W., Personal communication.

[4] SHUGAR, G., Personal communication.

Report of the NEW ENGLAND ASSOCIATION of CHEMISTRY TEACHERS

OFFICIAL BUSINESS

236th Meeting—May 11, 1946
Northeastern University
Boston, Massachusetts

THE meeting was opened by Dr. William C. White, *Director of the Day Division*, who brought the greetings of the University to the members of the Association. Dr. Blanche Daly, Assistant Professor of Biology at Northeastern University, spoke on "Nutrition Today and Tomorrow" and Dr. Arthur A. Vernon, the Head of the Chemistry Department at Northeastern University, spoke on "Some Aspects of Photochemistry." The last speaker of the morning was Mr. Cecil E. Hall, Research Associate in the Biology Department at the Massachusetts Institute of Technology, who gave an illustrated talk on the "Application of the Electron Microscope to Biology and Chemistry."

The business and annual meeting was held following lunch. The abstracted minutes follow:

Mr. Theodore C. Sargent, *Treasurer*, reported that although the fiscal year did not end until the first of July, 1946, he was safe in predicting that, for the first time in the history of the Association, there would be a balance on hand running into four figures. The balance on hand at the time of the meeting was $1230.29.

Professor Avery A. Ashdown, *Treasurer of the Endowment Fund*, reported a balance on hand of $1994.48.

Mr. Hoyt, for the Necrology Committee, presented the following resolutions on the death of Lt. Col. Wilbur E. Bradt:

Whereas: Lieutenant-Colonel Wilbur E. Bradt, one of our members, deferred for military duty since March, 1941, has passed on, and

Whereas: He has brought honor to this Association through his services as an artillery commander in the Pacific campaign, in the winning of the Legion of Merit award, the Silver Star with two oak leaf clusters, the Bronze Star Medal, and the Purple Heart with oak leaf cluster, and on account of this eminence and as head of the Chemistry Department of the University of Maine, and other services as a teacher of chemistry, be it

Resolved: That we, the members of the New England Association of Chemistry Teachers, express our high regard for Dr. Bradt and extend to his family our sincere sympathy in their bereavement. Be it further

Resolved: That a copy of these Resolutions be transmitted to his family, that a copy be deposited with the Secretary of this Association to be entered in the minutes of this meeting and finally filed with the necrology records of the Curator.

The report of the Membership Committee was as follows:

At the present time our active membership numbers 374 persons, the largest number of active members in the history of the Association. In addition we have 12 honorary members. It is impossible to report on the number of deferred members. Theoretically, there are still 33 on the list, but actually we have lost contact with many of these and are able to mail copies of the report section of the JOURNAL to ten only. The request in the JOURNAL for information on the whereabouts of those who are missing brought only two responses. We have lost through death and resignations this year 21 members, and we have added 39 new active members, 48 at the Summer Conference.

The Nominating Committee, consisting of Bernard A. Fiekers, *Chairman*, F. Harold Coburn, Eva M. Ruggli, and Carl P. Swinnerton, submitted the following nominations for officers of the Association for the year 1946–47:

President: Eldin V. Lynn
Vice-President: John R. Suydam
Secretary: Dorothy W. Gifford
Treasurer: Carroll B. Gustafson
Curator: Ralph E. Keirstead
Auditor: S. Walter Hoyt
Chairman of the Endowment Fund: Elbert C. Weaver
Chairman of the Northern Division: Lorne F. Lea
Chairman of the Central Division: Helen Crawley
Chairman of the Southern Division: Leallyn B. Clapp
Chairman of the Western Division: Jean V. Johnston

The nominees were elected.

After a vote of gratitude to the retiring officers for their services during the past year the meeting was adjourned.

Professor Lawrence H. Amundsen has been reappointed Editor of the Report for the year 1946–47 by vote of the Executive Committee.

NOTES

A matter of interest to members will be the action taken by the executive committee in deciding to contribute $10 to be used toward an award to some outstanding exhibitor in the Rhode Island Schools' Science Fair. The tremendous success of this Fair was due largely to the untiring efforts of one of our honorary members, Mr. J. Herbert Ward, and others of our members acted as judges.

Elbert C. Weaver and Laurence S. Foster have just had a high school text, "Chemistry for Our Times," published by McGraw-Hill.

Norris W. Rakestraw has left Brown University to become professor of chemistry in the Southern Section of the University of California and will be located at the Scripps Institution of Oceanography, La Jolla, California.

Lawrence H. Amundsen served as Acting Head of the Department of Chemistry at the University of Connecti-

cut for the past year and has been promoted from Associate Professor of Chemistry to Professor of Chemistry. Charles E. Waring, who was formerly Assistant Professor of Chemistry at the Brooklyn Polytechnic Institute and who for the past several years has served in various capacities in connection with several war research projects, has been appointed Head of the Department. David J. Blick has been promoted from Instructor in Chemistry to Assistant Professor of Chemistry.

NEW MEMBERS

Mr. Robert W. Card, Winchester High School, Winchester, Massachusetts
Sr. M. Claire, S.S.J., Regis College, Weston, Massachusetts
Rev. Leo J. Daly, St. Thomas' Seminary, Bloomfield, Connecticut
Sister Mary St. Blaise, Presentation of Mary Academy, Hudson, New Hampshire
Mr. H. Howard Lynch, Technical High School, Springfield, Massachusetts
Harvey R. Russell, 1 Yale Station, New Haven, Connecticut
Frank W. Hanson
Miss Helen Ross, Winsor School, Boston, Massachusetts

Eldin V. Lynn

Eldin V. Lynn, who has been elected President of the N.E.A.C.T. for 1946–47, is Professor of Chemistry and Chairman of the Department of Chemistry at the Massachusetts College of Pharmacy. He did his undergraduate and master's work at the University of Washington and took his Ph.D. degree at the University of Wisconsin. Dr. Lynn is author of "Organic Chemistry with Applications to Pharmacy and Medicine," published by Lea and Febiger, and of "Pharmaceutical Therapeutics," published by McGraw-Hill, and some 60 journal articles in the field of pharmaceutical chemistry. He is Chairman of the Committee on Research of the American Association of the College of Pharmacy and a member of the Revision Committee of the "United States Pharmacopoeia." Dr. Lynn's hobby is travel. He is, in fact, quite a world traveler and plans to go any place where he hasn't already been. He spent the past summer traveling extensively through the United States, Mexico, and Central America. As all of the members undoubtedly know, Dr. Lynn has held a number of important offices in the N.E.A.C.T. and has for many years been an active member.

LETTERS

To the Editor:

Through the courtesy of an editor friend I am privileged to see your journal regularly, and I often find matter of great interest in it. Some of the items I use in school and laboratory work. You certainly perform a valuable service in digesting chemical progress, for it is impossible to keep pace with modern researches and advances in chemistry, let alone to interpret them to students.

But I write mainly to express appreciation for your very understanding account of the food situation over here. As the writer in this issue (May, 1946, page 246) says, the rationing system is honestly administered and no one starves, but, owing to so many shortages, diet is uninteresting. Fats we miss most of all. This lack prevents our having many dishes that would vary our monotonous meals. Our children cannot understand why food is scarcer and less appetizing now that the war is over. I suppose we notice shortages more acutely because we expected immediate improvements. Of course there are improvements in other ways. There are no air raids, and it's no longer necessary to respond to the siren, don a blue uniform and tin hat, and go to wait for events we hoped would not happen, and when they did, work intensively at unpleasant and unaccustomed duties, perhaps until it was time to go straight to school for the day's work. In other words, we are less tired.

In the past schoolmaster scientists used to study little research problems arising from their work. When we return to normal, we hope to resume these minor investigations that made our routine more enjoyable. We also hope that in the future it will be easier to arrange interchange of both pupils and teachers so that we can come to know more of other peoples and so broaden our outlook and, if possible, lessen prejudice and promote the welfare of mankind.

LONDON, ENGLAND GERALD DRUCE

RECENT BOOKS

PHYSICAL CONSTANTS OF HYDROCARBONS. Volume III: Mononuclear Aromatic Hydrocarbons. *G. Egloff*, Director of Research, Universal Oil Products Company. Reinhold Publishing Corporation, New York, 1946. xiii + 661 pp. 15 × 23 cm. $15.

The present volume is the third of a series bearing this title, in which previous Volumes I and II have dealt with aliphatic and alicyclic compounds, respectively. The original plan to include all aromatics in Volume III has been modified because of the bulk of material found on the mononuclear series, and the polynuclear aromatics will appear in Volume IV. Constants recorded in the present volume include "melting points at all given pressures, boiling points at all pressures, densities at all temperatures, refractive indices of the sodium D, hydrogen α, β, and γ, and helium lines at all temperatures, angles of rotation at the sodium D lines at all temperatures, critical temperatures, critical pressures, critical densities, and sublimation points." An unusually complete coverage of the literature up to May, 1944, has been made to obtain these data, by consulting the complete files of *Chemical Abstracts*, Beilstein, Landolt-Bornstein, *Chemisches Zentralblatt* from 1900 through 1939 plus any more recent copies available, other secondary sources, and private information. "The original publications of the references thus located were then covered with the exception of a few which were unavailable or printed in languages other than English, French, German, Italian, Russian, and Spanish. . . . Approximately 5500 contained data suitable for this volume and Volume IV."

The introduction includes a section on the history of benzene and theories as to its structure, and a very good discussion of the methods used for critical evaluation of the data collected. In this compendium the author and his staff have chosen a statistical approach, perforce, since experimental verification of the data is frequently impossible. Unfortunately systematic errors are hard to detect by this system. The "most probable values" chosen for refractive index and melting points tend to be a little low, since many of the impurities found in an aromatic have a low refractive index and any impurity should lower the melting point. The "most probable value" for each property (shown in boldface type at the top of the appropriate column) represents the best value for all supposedly pure samples of each compound, but not always the best value for the pure compound.

A brief preface mentions the valuable data determined under various research projects of the American Petroleum Institute at the National Bureau of Standards, which were still on a "Restricted" basis when this book was completed. Many readers will be familiar with the data tables of A.P.I. Project 44, which have just recently been released for general use. For the lower members of each hydrocarbon series the A.P.I. tables are based on data accurately measured on preparations of high purity and checked against a complete literature review, and their selected properties for these particular compounds are more reliable than those reported here. However, the A.P.I. tables show only one value with no indication of how it was chosen and no original data. The present work has definite advantages for the ordinary user, and the bibliography given here for each compound will be particularly useful in looking up the chemistry of complex hydrocarbons.

The use of structural formulas throughout is very helpful, even though expensive to print. Structural relationships which could not possibly be suggested by systematic nomenclature are made clear. While it may seem in some cases that the most space is spent on the least important compounds, the author has taken great pains to make the tables complete, and his work will be most appreciated when obscure information is needed.

The publication of this work will save an enormous amount of library time for those interested in hydrocarbon research. It points clearly to places where compounds in a given series are missing or poorly characterized, and further research is needed. In spite of its expense, the present volume should be widely read as a reference book and as a guide to research wherever such work is being done.

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QUANTITATIVE ORGANIC MICROANALYSIS. Based on the methods of *Fritz Pregl*, University of Graz. Fourth English Edition. Completely revised and edited by *Julius Grant*. The Blakiston Company, Philadelphia, 1946. vii + 238 pp. 94 figs. 11 tables. 15.5 × 23.5 cm. $5.00.

The previous editions of Pregl have been essentially literal translations; however, Dr. Grant now states in his preface, ". . . it has been felt that the time has come for (the text) to be thoroughly revised, both in scope and method of presentation, and there will be few who will disagree with the conclusion that one of the most desirable of innovations is the introduction into it of a more 'international' character."

In this revision, the text has been considerably condensed and the methods are now presented as an orderly sequence of subsections. Pregl's methods have been retained and adapted wherever they were thought to be still the most reliable and convenient, but modifications introduced by more modern workers are often included. Dr. Grant has added some new sections, including those on volumetric work, colorimetry, determinations of physical constants, general microchemical technique, and gas analysis. In some cases these additions consist only of brief mention of the methods involved. This is particularly true with the section on colorimetry.

In general, the book represents a distinct improvement over the earlier editions. An intelligent student could usually be expected to follow the directions without difficulty; however, there are several places where an expert might not be confused, but where the beginner will certainly need careful guidance from his instructor. With regard to general style, the author does little to counteract the oft-repeated claims that chemists do not write good English.

Approximately 150 of the 322 references are to work which has been published since 1935, when the last English edition of *Pregl* appeared. The work of the A.C.S. committee on apparatus specifications has been listed. Two cases of misuse of *Ibid* in the bibliography were noted: thus Reference 7, p. 15, should be to *Ind. Eng. Chem., Anal. Ed.*, and Reference 3, p. 109, should be to *Mikrochem.* The author of Reference 10, p. 85, should be Nichols, M. L.

Numerous typographical errors appear. Those detected by this reviewer were, with a single exception, ones which should cause only momentary confusion. On p. 60, however, it should be indicated that tin is determined as SnO_2 and not SnO. The figures and illustrations are only fair and Figure 26 is shown in an inverted state. The indexes seem to be reasonably complete.

The criticisms listed above do not detract from the fact that this text deserves to maintain the high place previously given to English editions of Pregl. The reviewer would like to have seen included more complete directions for the use of "dry ice" as a source of carbon dioxide, greater attention to potassium hydrogen iodate as a direct titration agent, and more systematic treatment of the time factor in the various determinations. From the teacher's standpoint it is unfortunate that the calculations are spoon-fed in almost every case. It is hoped that in future editions when paper is more available, logarithmic and gas reduction tables might be included.

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